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THE HYDROLYSIS OF ORGANIC PEROXIDES AND PERACIDS.

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In cases of autoxidation, hydroperoxide has been frequently met with. Kingzett[2] and Löw[3] have shown that in the case of oxidized turpentine oil the active oxygen is not originally present in the form of hydroperoxide, and Engler and Weissburg[4] have further pointed out the fact that in all cases where hydroperoxide has been observed among the products of autoxidation its presence could be explained by assuming a secondary reaction of water with the original product. They look upon this change not as a direct oxidation process but as a hydrolytic one, *i. e.*, one brought about by the interaction of the substance in question with hydrogen and hydroxyl ions. They call attention to the fact that if benzoic peroxide be added to a solution of titanic acid in sulphuric acid, the latter, in time, takes on the yellow color produced by hydroperoxide, and they find that acetic peroxide gives this coloration almost immediately. They attribute these colorations to the formation of hydroperoxide.

[1] Parke, Davis & Co. Fellow in the University of Michigan.
[2] J. Chem Soc. (London), **12**, 511; **13**, 210.
[3] Chem. Centrbl., 1870, p. 821.
[4] Ber. d. chem. Ges., **31**, 3047.

Brodie,[1] however, makes the statement that with water the peroxides separate into free acid and oxygen.

Baeyer[2] has saponified benzoic peroxide with sodium ethylate, and acetic peroxide with sodium hydroxide. In the former case he isolated benzoperacid, and in the latter showed that the resulting product had acquired the properties of a peracid. He also points out that benzoic and acetic benzoic peroxides are substances without action upon solutions of potassium iodide or indigo, and without odor, and concludes that the acquisition of such properties by these substances is probably to be attributed to a hydrolytic change in which peracids are formed.

Wolffenstein[3] has found that the peroxides of acetone and mesityl oxide separate hydroperoxide on warming with dilute sulphuric acid, and Baeyer[4] has further observed that phthalmonoperacid gives rise to hydroperoxide on heating the solution.

Numerous authors have noted the formation of hydroperoxide by the action of alkalies upon peroxides.

Freer and Novy[5] have studied the action of water upon benzoic acetic peroxide, and have found that the active oxygen gradually goes into solution, while considerable quantities of benzoic peroxide are formed.

The most interesting and extensively investigated organic peroxides are those of the acids. These substances are to be considered as derivatives of hydroperoxide, and those which have been thoroughly investigated are found to belong to one of two classes:

1. Peroxides, in which both of the hydrogen atoms in a molecule of hydroperoxide are replaced by acid radicals.

2. Peracids, in which only one of the hydrogen atoms is so replaced.

With the object of discovering the exact nature of the changes which these bodies undergo with water, and of giving a general expression to our results, we have carefully in-

[1] Ann. Chem. (Liebig), Suppl., **3**, 211.
[2] Ber. d. chem. Ges., **33**, 1569.
[3] *Ibid.*, **28**, 2265.
[4] *Ibid.*, **34**, 762.
[5] This JOURNAL, **27**, 161

vestigated the behavior of several representative peroxides and peracids. Our work enables us to draw the following conclusions:

1. Acid peroxides are completely hydrolyzed by water into acid and peracid. The time taken to complete the change varies, of course, with the nature of the peroxide and with its solubility in water. A 5 per cent solution of acetic peroxide is completely changed in the course of forty-eight hours, while with butyric or crotonic peroxides the change is very much slower. With benzoic peroxide it is so slow as to be scarcely detected in the course of several days. This change is a complete one in all cases which we have investigated, that is, the reaction is not a reversible one:

$$R.OO.R + H_2O = ROH + R.OO.H.$$

In case the peroxide is not homogeneous the hydrolysis may take place in two ways:

$$R.OO.R' + H_2O = ROH + R'.OO.H,$$

or

$$R.OO.R' + H_2O = R.OO.H + R'OH.$$

In the case of benzoic acetic peroxide the change was found to take place almost, if not altogether, completely in one way.

In the hydrolysis of peroxides of this class other products are met with, owing to a secondary reaction of the peracid first formed with the original peroxide. We have found that peracids in aqueous solution are extremely reactive toward substances capable of hydrolysis, such as acid chlorides, anhydrides, and peroxides:

$$ROR + R'.OO.H = R.OO.R' + ROH;$$
$$R.OO.R + R'.OO.H = R.OO.R' + R.OO.H.$$

In all cases a peroxide is formed, together with an acid or a peracid. In case this peroxide is formed faster than it is hydrolyzed, it is evident that it will accumulate. In this way the less soluble and more slowly hydrolyzed homogeneous peroxide will be formed as a product of hydrolysis of a mixed peroxide, and the peracid which results from the reaction will be found in the solution.

2. Peracids are hydrolyzed into acid and hydroperoxide:

$$R.OO.H + H_2O = ROH + H.OO.H.$$

The change is a much slower one than the corresponding peroxide hydrolysis and, following the general law of hydrolytic processes, takes place much more rapidly in acid solution. This change is also a non-reversible one.

Acetic Peroxide.

Preparation.—Brodie[1] first prepared this substance by the action of hydrated barium peroxide upon acetic anhydride, the former being gradually added to a cooled ethereal solution of the latter. The yield which he obtained was very poor. Nef[2] prepared it by the action of pure hydroperoxide upon acetic anhydride, and Baeyer[3] makes the observation that it is formed by adding acetic anhydride to an aqueous solution of hydroperoxide. In working with considerable quantities of this substance we have found the method of Nef too laborious and that of Baeyer unsatisfactory as to yield. We have again studied the action of barium dioxide upon acetic anhydride, and have been surprised to find that under proper conditions nearly a theoretical yield of the acetic peroxide may be obtained. Twenty-two and a half grams of comparatively good barium dioxide (94 per cent) were covered with 30 cc. of water and shaken for a few minutes with cooling. Twenty grams of acetic anhydride were added to 100 cc. of ether and cooled to 0°. The suspension of barium dioxide was then gradually added, with shaking, during the course of five minutes. The mixture was kept cooled to 0° and shaken for about fifteen minutes, when the dioxide had about disappeared. The ethereal layer was then removed by decantation, dried for several hours over calcium chloride, and the solvent then removed in a vacuum. The peroxide begins to crystallize from the cold, concentrated solution, and finally remains as a pure crystalline residue. It may be recrystallized from ligroin by cooling, in a freezing-mixture, a

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), **298**, 287.
[3] Ber. d. chem. Ges., **33**, 1569.

solution saturated at room temperature. Owing to the danger of spattering during the removal of the last portion of ether, it is advisable, on account of the extreme explosiveness of the substance, to dissolve the concentrated ethereal solution in ligroin and allow the peroxide to crystallize in a freezing-mixture. The yield was 8.8 grams. As the peroxide is probably formed according to the equation

$$2(CH_3CO)_2O + BaO_2 = Ba(C_2H_3O_2)_2 + C_4H_6O_4,$$

this amount represents 76 per cent of the total possible yield. Almost as good a yield may be obtained by using the cheaper and less pure barium dioxide, although in this case it is better to use more than the calculated amount, owing to the slow solubility of portions of the commercial article. If the solution be kept well cooled the yield is not greatly decreased by using excess of the dioxide. The pure peroxide liberates the theoretical amount of iodine from a solution of potassium iodide (best in 20 per cent acetic acid).

If the peroxide is dissolved in excess of N/10 potassium hydroxide and the solution heated on a water-bath for ten minutes, on titrating the excess of hydroxide the amount used will be found to correspond to 2 molecules for every molecule of peroxide.

The pure peroxide, shaken with water at 25° for five minutes, yielded a 0.935 normal solution of active oxygen. When the shaking was continued for ten minutes a 0.950 normal solution was obtained. At this rate of hydrolysis the real solubility may be placed at 0.920 normal, or 54.2 grams per liter.

As previously stated, this substance, like all acid peroxides having an appreciable solubility in water, liberates iodine from a solution of potassium iodide. The action of these substances in neutral or slightly acidulated solution is very slow, but is greatly increased in rapidity in more strongly acid solution. In this case, however, it is necessary to make a correction for the amount of iodine liberated from a blank solution under the same conditions. It is generally best to use acetic acid to acidulate with, as the solubility of the peroxides is thereby greatly increased.

If potassium iodide is added to a slightly acidulated, freshly prepared solution of acetic peroxide, there is no immediate liberation of iodine. On standing, however, the latter appears in the solution in gradually increasing concentration and the reaction is complete in three or four hours. If, however, the solution of peroxide is allowed to stand twenty-four hours before the addition of potassium iodide, its behavior is markedly different. In this case the liberation of nearly the entire amount of iodine takes place immediately. As will be shown later, the change which has produced this difference in behavior requires at least twenty-four hours to complete itself. As already noted, however, the liberation of iodine is complete in three or four hours in a non-hydrolyzed solution. This indicates that either a condition of equilibrium exists between the factors of the reaction, permitting the reaction to go to completion much more quickly by the removal of one of the products, or that the unchanged peroxide is itself an oxidizing agent. However, from a saturated solution of acetic peroxide which had stood a week, it was impossible to extract any of the unchanged substance by means of ligroin. The peroxide is more soluble in ligroin than in water. A small amount of active oxygen is taken up by the ligroin, but the former oxidizes potassium iodide immediately, and is therefore due to acetperacid. As the presence of small quantities of unchanged peroxide would be indicated by a further slow liberation of iodine, it may be concluded that the change is a complete one. From this and the similar behavior of other peroxides, it is to be assumed that they are themselves oxidizing agents.

This gradual change which a solution of peroxide undergoes may be followed in a rough way by noting, from time to time, the amount of iodine liberated immediately, the iodine being estimated by means of a N/10 solution of sodium thiosulphate. Of a freshly prepared solution, 5 cc. required a total of 20.2 cc. N/10 thiosulphate: after four hours the immediate liberation of iodine required an average of 9.7 cc.: at the end of eight hours, 14.6 cc.: after twenty-two hours, 19.3 cc. The solution stood at a temperature of 20°. The titration was

performed as quickly as possible after adding the potassium iodide, but even then the values obtained are not to be considered absolute, owing to the oxidizing action of the unchanged peroxide. The numbers indicate the general course of the change, however. A similar experiment with the analogously constituted propionic peroxide shows the progress of the change much more exactly.

Cryoscopic Determination.—0.655 gram acetic peroxide was dissolved in 25.703 grams water in an ordinary Beckmann apparatus. A lowering of 0°.444 was produced.

Molecular Weight.

Calculated.	Found.
118	109

The solution was then allowed to stand at 20° and additional readings of the freezing-point were taken from time to time:

After	8	hours, additional lowering		0°.223
"	20	"	"	0°.338
"	24	"	"	0°.343
"	32	"	"	0°.363
"	44	"	"	0°.380
"	50	"	"	0°.377

Some little time was spent in dissolving the substance and getting conditions for the first reading, so that the latter is a little large, accounting for the low molecular weight found. At the end of two days there was little change in the freezing-point on further standing. The total depression of the freezing-point is 0°.821. The calculated depression caused by a hydrolysis of 1 molecule of peroxide into 2 molecules is 0°.820. It might not be expected that these numbers should agree quite so well, as it will be seen later that further changes take place in the solution. The experiment is in good agreement with the one in which the immediate liberation of iodine was estimated from time to time, and clearly demonstrates that the primary change is one in which 2 molecules are produced from one of the peroxide. As it will be shown further on

that one of these substances is acetperacid, the change may be expressed as follows :

$$CH_3CO.OO.COCH_3 + H_2O = CH_3CO.OO.H + CH_3COOH.$$

The Formation of Hydroperoxide.—If a saturated solution of acetic peroxide be subjected to the tests for hydroperoxide, only negative results are obtained, *i. e.*, chromic acid is not oxidized to perchromic acid, and a solution of titanic acid in dilute sulphuric acid is not colored. The latter solution, however, soon becomes yellow on standing, the more quickly, the more sulphuric acid is present, other conditions being the same. The rapid formation of hydroperoxide in this case is to be attributed to the hydrolytic influence of the sulphuric acid. In numerous cases in the literature, peroxides are described as responding to this test. It is highly probable that all such cases are due to the hydrolytic development of hydroperoxide due to the use of too strong sulphuric acid in preparing the titanic solution. None of the peroxides which we have examined respond to this test except on standing. On the other hand, the delicacy of the perchromic acid test for hydroperoxide is greatly decreased by the use of mineral acid, and for this reason it is more reliable, although not so delicate. It is easy to detect 1 part of hydroperoxide in 100,000 parts of water by covering the solution with ether, cooling, adding a grain of potassium bichromate, and then very dilute sulphuric acid drop by drop until the maximum coloration is produced. After the solution of acetic peroxide has stood for two hours, there are evidences of the formation of hydroperoxide by a slight immediate coloration with titanic acid. At the end of three hours a decided test is obtained with chromic acid. The first change, *i. e.*, the hydrolysis of acetic peroxide, has been shown to be practically complete in about two days. At the end of this time 93 per cent of the active oxygen in the solution causes immediate liberation of iodine. As it has already been shown that the solution at this point contains practically no acetic peroxide, this remaining active oxygen is to be attributed to hydroperoxide, which, like the acetic peroxide, liberates iodine very slowly in dilute acetic acid solution. The amount of hydroperoxide continues to increase on

standing, until at the end of a month nearly the entire active oxygen content of the solution is present in this form. It is evident, then, that the hydroperoxide results from the hydrolysis of the acetperacid,

$$CH_3CO.OO.H + H_2O = CH_3COOH + H.OO.H.$$

The following table shows the stability of a solution of acetperacid and the rate at which it is hydrolyzed into hydroperoxide. The numbers in the first column indicate the immediate liberation of iodine by 5 cc. of the solution, estimated as quickly as possible by a solution of N/10 thiosulphate; they represent acetperacid. The numbers in the second column indicate the total active oxygen in 5 cc. of the solution, due to acetperacid and hydroperoxide. In the third column are placed the differences between the total and immediate iodine representing hydroperoxide. Experiments with benzoperacid and hydroperoxide showed that, in dilute acetic acid, the two substances may be estimated in the presence of each other by this method:

Time in days.	Cc. thiosulphate. Immediate.	Cc. thiosulphate. Total.	Difference.
0	0.0	40.2	
2	37.3	40.0	2.7
3	35.1	39.3	4.2
4	32.0	37.5	5.5
5	29.0	36.7	7.7
9	24.7	35.5	10.8
15	18.2	34.3	16.1
22	11.8	31.4	19.6
30	5.4	28.0	22.6
34	3.4	26.5	23.1

Further Evidence of the Presence of Acetperacid.—From the behavior of the hydrolyzed solution toward potassium iodide, and by comparison with the similar behavior of the benzoperacid of Baeyer, it has been assumed that acetperacid was one of the products of hydrolysis. The following experiments conclusively decide this point:

Action of Acetic Anhydride.—An aqueous solution of acetic peroxide was allowed to stand twenty-four hours. It was then

extracted several times with ligroin, by which means small quantities of unchanged peroxide were removed, the hydrolyzed product being much more soluble in water and less soluble in ligroin than the peroxide. Two cc. of the solution then liberated iodine, requiring 14.2 cc. N/10 thiosulphate immediately and 0.8 cc. additional, due to hydroperoxide and unchanged acetic peroxide. Fifty-one cc. of this solution, representing 2.1 grams of acetic peroxide originally, were placed in a flask, cooled to 15°, and 4 grams of acetic anhydride added and dissolved by shaking. The solution was kept cooled to 15°. One cc. was removed at intervals (5 cc. in all), and the "immediate" titer was found to gradually decrease from its original value of 6.4 to 1.2 in about one-half hour, the total active oxygen content of the solution remaining the same (decreased slightly by the dilution with acetic anhydride). After this time it began to slowly increase again. After two hours it was extracted several times with ligroin. On evaporating the solvent and cooling, acetic peroxide crystallized out. 0.0764 gram analyzed for active oxygen required 12.7 cc. N/10 thiosulphate; calculated 12.9 cc. The amount of peroxide removed by extracting four times with 0.5 volume of ligroin was 0.7 gram, and an additional amount remained in the solution.

It will be recalled that before the addition of acetic anhydride the solution had been thoroughly extracted with ligroin, and only a very small amount of peroxide was obtained. Further, that the amount of hydroperoxide in the solution would account for the formation of only a trace of acetic peroxide. The following reaction, therefore, took place:

$$CH_3CO.OO.H + (CH_3CO)_2O = CH_3CO.OO.COCH_3 + CH_3COOH.$$

Action of Benzoyl Chloride.—Twenty cc. of an aqueous solution of acetic peroxide (1 cc. required 6 cc. N/10 thiosulphate) stood twenty-four hours. To the solution were added 2 grams of benzoyl chloride and an excess of sodium acetate. The mixture was shaken in a flask at 25° for ten hours, in which time the product had solidified. The solid product was dissolved

in ether and shaken out with a solution of sodium carbonate. On evaporation of the ether a crystalline residue remained which still retained the odor of benzoyl chloride, and was allowed to lie exposed to the air until this had disappeared. The residue consisted of a mixture of benzoic and benzoic acetic peroxides, the difference in their solubility in ligroin permitting of a separation. The latter substance separated from the mother-liquor with difficulty, owing to the presence of an oily impurity. After crystallizing several times, the melting-point could not be raised beyond 36° (Baeyer, 38° to 39°). At this point there was not enough of the substance left for analysis, but there is little doubt in our minds as to its identity. The original residue consisted of about 25 per cent of the benzoic acetic peroxide, estimated in dilute acetic acid with potassium iodide and thiosulphate. The benzoic peroxide does not liberate iodine in dilute acetic acid. The benzoic acetic peroxide was probably formed according to the following equation:

$$C_6H_5COCl + CH_3CO.OO.H = C_6H_5CO.OO.OCCH_3 + HCl.$$

The formation of benzoic peroxide here, in such large quantities, is noteworthy and interesting. We are unable at present to explain the process by which it is formed.

Acetperacid.—The isolation of this substance from an aqueous solution containing acetic acid presents great difficulties, and we have not been successful in our attempts to do this. As the chief interest in this substance lies in its oxidizing properties, and as the solution as formed is quite well adapted for its use in this respect, there is no special need for its isolation. A few of the striking characteristics of the solution are as follows: Indigo is bleached slowly, more rapidly with the addition of dilute sulphuric acid. A weak solution of litmus is not decolorized by a large excess of the oxidizing agent in twelve hours. Chlorine is liberated from a dilute solution of hydrochloric acid. A drop of potassium permanganate is unaffected in a large excess of the solution weakly acidulated with sulphuric acid. In strong acid solution (1 : 5) it is soon decolorized, owing to its rapid hydrolysis into

hydroperoxide. If a grain of manganous acetate be added to an excess of the solution, a red coloration is produced which is somewhat obscured by the formation of manganese dioxide. If dilute sulphuric acid be previously added, the solution assumes the characteristic color of permanganic acid, and no manganese dioxide is formed unless considerable of the manganous salt is added. In strong sulphuric acid solution (1 : 5) the formation of permanganic acid is prevented. If potassium permanganate be added drop by drop to a solution containing both acetperacid and hydroperoxide, weakly acidulated with sulphuric acid, it is quickly decolorized until the hydroperoxide is destroyed. At this point the manganous salt begins to be reoxidized to permanganic acid, and the solution is soon deeply colored.

An attempt to estimate a known amount of hydroperoxide in the presence of a solution of acetic peroxide, which had stood for two hours, gave a result a little low, as might be expected, for, in the time required to make the titration, a small amount of the manganous salt formed by oxidation of hydroperoxide is reoxidized by the peracid to permanganic acid, thus decreasing the required amount of the latter.

The solution of acetperacid does not oxidize alcohol, which is shown by the fact that the amount of peracid in a solution to which alcohol had been added had not decreased on standing twenty-four hours. The same result was obtained by adding crotonic acid to a solution.

The solution gives no precipitate on addition of the acetates of silver, lead, mercury, or copper. With silver oxide and lead monoxide a rapid evolution of oxygen occurs. A solution of basic lead acetate shows the same behavior. Manganese dioxide shows no catalytic action but is oxidized to permanganic acid.

As the simplest representative of the organic peracids, it is quite probable that this substance will be found suitable for oxidizing purposes in certain cases, as has already been the case with the similarly constituted sulphuric peracid (Caro's reagent).[1] Its suitability for such purposes lies in the follow-

[1] Ber. d. chem. Ges., 32, 1676, 3625.

ing facts: (1) It is easily prepared; (2) a very concentrated solution may be made by continued hydrolysis of an excess of the peroxide; (3) it is an organic oxidizing agent and the reduction-product is unobjectionable.

As has already been observed, the acetic peroxide when caused to explode does so with great violence. During our work with this substance we have never observed an explosion except when it was heated or subjected to unnecessary friction. To prepare the substance pure, it is not necessary to handle it as the crystallization may be brought about in a flask, the mother-liquor removed by decantation, and the crystals washed and dried in a vacuum without removing them from the flask. We have employed this method repeatedly without accident. In cases where the presence of ether is unobjectionable, the solution of acetperacid may be made by dissolving in water the concentrated ethereal solution of the crude product.

Propionic Peroxide.

Preparation.—The method employed in making acetic peroxide was used also in this case. Eight and a half grams of propionic anhydride were dissolved in 100 cc. of ether and cooled to 15°. Six grams of 95 per cent barium peroxide were suspended in 40 cc. of water, cooled to 15°, and added to the ethereal solution. On shaking for fifteen minutes the barium peroxide was dissolved. The maximum amount of propionic peroxide was not present in the solution until a total of 7.5 grams of barium peroxide had been added. Until this point was reached the solution still contained unchanged anhydride (found by comparing the amount of N/10 potassium hydroxide required by 1 cc. of solution with amount of N/10 thiosulphate required.) At the point of maximum yield the anhydride had disappeared, and the addition of more barium peroxide decreased the amount of propionic peroxide. The necessity for using an excess of barium peroxide is thus found, and that the yield of propionic peroxide (4 grams) does not equal the theoretical is also accounted for. The reaction, therefore, takes place according to the following equation:

$$2C_6H_{10}O_3 + BaO_2 = C_6H_{10}O_4 + BaC_6H_{10}O_4.$$

The ethereal solution was dried over calcium chloride, the ether evaporated in a vacuum, and the last traces completely removed by means of a current of dry air at 35° in a vacuum. The resulting product was analyzed as follows: The active oxygen was estimated by dissolving in 80 per cent acetic acid containing potassium iodide, and allowing to stand for one-half hour for complete liberation of the iodine. It was then diluted and the latter estimated by N/10 thiosulphate. A blank experiment was then made under the same conditions and the correction applied.

As a substitute for the difficult elementary analysis, the amount of potassium hydroxide required to convert a known amount into potassium propionate was determined. This method has already been spoken of under acetic peroxide. The substance was dissolved in an excess of N/10 potassium hydroxide, heated for ten minutes on a water-bath, and the excess of potassium hydroxide then determined by titration.

The residue of propionic peroxide, on removal of the ether, gave active oxygen and acid values both a little high. This could be accounted for only by assuming the presence of a small amount of acetic peroxide. This was confirmed by repeatedly shaking the product with small portions of water. The first washings contained much more active oxygen than the latter, the content of which soon became constant, representing the solubility of the pure propionic peroxide. Ten cc. required 10.9 cc. N/10 thiosulphate.

The saturated solution is therefore 0.109 normal and contains 15.9 grams per liter.

The washed product was again taken up with ether and dried. On complete removal of the solvent it gave analytical results showing that it was pure propionic peroxide:

0.1595 gram required 21.7 cc. N/10 thiosulphate; calculated 21.85 cc.

0.1395 gram required 19.0 cc. N/10 potassium hydroxide; calculated 19.1 cc.

The presence of a more highly oxidized form was at first suspected in the crude product. This is made impossible by

the fact that the potassium hydroxide and thiosulphate values, while both high, were exactly the same. The acetic peroxide was probably formed from acetic anhydride present as an impurity in the propionic anhydride employed.

The pure propionic peroxide is miscible with all the ordinary solvents. When heated to 80° a slow effervescence sets in, which continues until the decomposition is complete. Hydrocarbons and carbon dioxide are evolved, and the residue is a gum which dissolves completely in sodium carbonate and is again precipitated on acidifying. When subjected suddenly to a high temperature the peroxide explodes, but without the violence and detonation of acetic peroxide. At —20° it could not be induced to solidify. Owing to its instability, no attempt was made to distil it.

Hydrolysis.—In the case of acetic peroxide a rough idea of the course of its hydrolysis was obtained by determining the immediate liberation of iodine from time to time. In the case of propionic peroxide the progress of the reaction is shown quite nicely by this method. In dilute acetic acid the unhydrolyzed peroxide affects potassium iodide very slowly, so that by working quickly it is possible to estimate the amount of peracid in a solution accompanied by peroxide, without much error due to the latter.

The following table shows the behavior of a solution of propionic peroxide at a temperature of 20°. Five cc. of the solution required a total of 10.8 cc. N/20 thiosulphate. The numbers under "immediate iodine" represent the amount of thiosulphate required by 5 cc. of the solution from time to time. The relative values of the reaction-constant,

$$\left(K = \frac{1}{t} \log \frac{a}{a-x}\right),$$

have been calculated, assuming the reaction to be of the first order. In the first three determinations there is a remarkably good agreement in this value, as an error of 0.1 cc. in the titration numbers is sufficient to account for the variation. The lowness of the fourth value is probably due to the forma-

tion of hydroperoxide in the more concentrated solution of peracid.

Time in hours.	Immediate iodine. cc.	Reaction-constant.
3.0	3.0	471
6.5	5.4	463
11.5	7.6	459
23.0	9.8	449

The reaction is to be expressed as follows:

$$C_2H_5CO.OO.COC_2H_5 + H_2O = C_2H_5CO.OO.H + C_2H_5COOH.$$

After twenty-four hours hydroperoxide may be detected in the solution. In its chemical behavior propionic peracid is not to be distinguished from acetic peracid.

Crotonic Peroxide.

Crotonic Anhydride.—The general method proposed by Autenrieth[1] was employed with very satisfactory results. One hundred grams crotonic acid were boiled with 350 grams acetic anhydride for twenty-four hours, with reflux condenser. The acetic acid and excess of anhydride were then distilled off under diminished pressure. The residue was taken up with ether and shaken out with the requisite amount of sodium carbonate for removal of unchanged acid. It was then dried over calcium chloride and, after distilling off the solvent, was fractionated under diminished pressure. About 60 grams of practically pure anhydride, boiling within 4° to 5°, were finally obtained. The amount of mixed anhydride formed was small. The highly purified crotonic anhydride boils at 128° to 130°, under 19 mm., with slight decomposition. Its specific gravity at 29°, compared with water at the same temperature, is 1.0338. It does not solidify at —15°.

Analysis: 0.1734 gram substance gave 0.3956 gram CO_2 and 0.1019 gram H_2O.

	Calculated for $C_8H_{10}O_3$.	Found.
C	62.34	62.21
H	6.49	6.53

[1] Ber. d. chem. Ges., 34, 168.

0.1000 gram required 26.0 cc. N/20 potassium hydroxide to neutralize; calculated 26 cc.

Preparation of Peroxide.—Seven and eight-tenths grams anhydride were dissolved in 100 cc. ligroin and added to 3.4 grams of hydroperoxide in 8 per cent solution. This mixture was cooled to 15°, and a saturated solution of barium hydroxide added in portions of 10 cc., shaking after each addition until the barium dioxide had disappeared. The mixture was kept cooled to 15°, and the course of the reaction was followed by estimation of the active oxygen content of 1 cc. of the solution from time to time. The latter showed a maximum value after the addition of 100 cc. (3.14 grams) of barium hydroxide. There was present in the solution at this point active oxygen to account for 3.9 grams of crotonic peroxide. On removing the ligroin solution and partially evaporating the solvent, the peroxide separates as crystals on cooling. Only about 2 grams of these crystals were obtained, the remaining product separating as an oil. This oil is probably an oxidation-product of the unsaturated crotonic anhydride in alkaline solution, for we have observed that hydroperoxide and peracids are much more powerful oxidizers in the presence of alkalies than in neutral or acid solution. The crystals which separated from the ligroin solution were practically pure. The pure substance consists of needles and irregularly shaped plates, and melts at 41°. It is odorless and explodes gently on heating. It does not decompose on long standing. It is soluble in all of the ordinary solvents.

The active oxygen was determined by dissolving in 10 per cent acetic acid and adding a solution of potassium iodide acidulated with dilute sulphuric acid. A blank experiment was made and the correction applied.

0.1182 gram substance required 13.8 cc. N/10 thiosulphate; calculated 13.9 cc.

0.1249 gram treated with excess of N/10 potassium hydroxide required 30.7 cc. to neutralize; calculated 29.4 cc.

This method of analysis is evidently not applicable in the case of an unsaturated peroxide. The elementary analysis was therefore made.

0.1328 gram substance gave 0.2737 gram CO_2 and 0.0705 gram H_2O.

	Calculated for $C_8H_{10}O_4$.	Found.
C	56.47	56.20
H	5.88	5.81

Hydrolysis.—This substance was selected on account of its being crystalline, with the intention of isolating the peracid formed. The slowness with which it hydrolyzes, however, renders it unsuitable for such study.

An excess of peroxide was added to water contained in a glass-stoppered flask and shaken at 25° for several days. The progress of the hydrolysis was ascertained by removing 25 cc. of the solution at intervals and determining the immediate liberation of iodine. The difference between immediate iodine and total iodine is seen to be the same in each case, representing the solubility of the unchanged peroxide, which remains constant. There is also seen to be a regular increase in the amount of peracid. The latter, therefore, appears to have no oxidizing action on the unsaturated carbon atoms.

Time in days.	Immediate iodine. Cc. N/10 thiosulphate.	Total iodine. Cc. N/10 thiosulphate.
2	1.35	4.1
4	2.7	5.5
8	5.2	7.9

A portion of the solution removed, after standing for one month, had lost only one-fourth of its active oxygen, which was then present almost entirely as peracid. At this time hydroperoxide could just be detected by means of the chromic acid test.

Another completely hydrolyzed solution of 0.3 gram peroxide in 50 cc. water was extracted with ligroin, thereby removing only a trace of peracid. On extracting twice with ether the peracid was completely removed, together with crotonic acid. On evaporating the ether a crystalline residue remained, which possessed the characteristic peracid odor.

Benzoic Acetic Peroxide.

The substance dissolved in dilute acetic acid liberates the

theoretical amount of iodine from potassium iodide. Its solubility in water at 25° amounts to 0.639 gram per liter.[1] This solution, on standing, suffers not only a change to peracid, as noted by change in the amount of iodine liberated immediately, but soon becomes turbid, owing to the separation of the insoluble benzoic peroxide. By adding an excess of the peroxide to water and shaking the mixture to keep the solution saturated, the benzoic peroxide gradually accumulates, while the soluble products remain in the solution. In this way a more concentrated solution of the latter is obtained, suitable for study.

Four grams of the peroxide were added to 250 cc. water and shaken at 25°. At intervals, given in the table below, a portion of the solution was filtered through glass wool, 10 cc. of the filtered solution removed, and its immediate and total liberation of iodine estimated with N/10 thiosulphate. After forty-two hours the presence of hydroperoxide was plainly shown by the chromic acid test. This accounts for the gradual increase in the amount of "additional iodine," which is made up of unchanged peroxide and hydroperoxide. The numbers in the column under "immediate iodine" give a general idea of the rate of formation of peracid. As this experiment was continued through a considerable space of time and peracids in solution are unstable, they represent less than the total amount of peracid formed.

The rate of hydrolysis, as represented by the rate at which the solution takes on active oxygen, is found to increase slowly during the course of the experiment, probably owing to the increased solubility of the peroxide and to the catalytic action of the acid formed.

Time in hours.	Immediate iodine.	Additional iodine.
21	3.8	0.8
42	8.0	0.9
52.5	10.3	1.0
73.5	14.3	1.3

The following experiments were performed with accurately weighed amounts of pure peroxide:

[1] Freer and Novy: *Loc. cit.*

1. 0.5180 gram was added to 50 cc. water and shaken in a sealed flask at 25° until the change was complete. As previously mentioned, a solution of benzoic acetic peroxide becomes decidedly turbid on standing, and this fact made it possible to ascertain the completeness of the reaction. After four days the flask was opened, the residue carefully filtered and washed, the washings being added to the filtrate. The residue consisted of 0.1726 gram pure benzoic peroxide (m. p. 107°.5). (As the filtration was made through glass wool the benzoic peroxide was not conveniently determined by estimating the active oxygen. Experiments with pure benzoic peroxide showed the following method to be accurate: The peroxide is dissolved in 80 per cent acetic acid containing potassium iodide and allowed to stand one hour, when the solution is diluted and the iodine estimated. A correction, determined by a blank experiment under the same conditions, is then applied.) The filtrate was found to require 39.5 cc. N/10 thiosulphate for "immediate" iodine and 2.5 cc. for "additional." The total active oxygen obtained from the products of hydrolysis amounted to 0.0028 gram-molecule of the original peroxide, while 0.00288 gram-molecule had been taken. The loss is due to the instability of the solution of peracid. The per cent of active oxygen which separated as benzoic peroxide was 24.7.

2. 0.5100 gram was added to 100 cc. water and the previous experiment repeated. It was removed in thirty hours. 0.1416 gram benzoic peroxide was formed. The solution required 43.8 cc. N/10 thiosulphate. The total active oxygen recovered amounted to 0.00277 gram-molecule, while 0.00283 gram-molecule had been used. The per cent represented by benzoic peroxide was 20.6.

3. 0.6211 gram was shaken with 250 cc. water, twenty-four hours being necessary to complete the change. 0.1510 gram benzoic peroxide was formed. The solution required 54.8 cc. N/10 thiosulphate. A total of 0.00336 gram-molecule was recovered while 0.00345 had been used. 18.1 per cent of the active oxygen separated as benzoic peroxide.

It will be noted that the amount of benzoic peroxide formed

is decreased by using more water. From this it may be inferred that the rate of formation of this substance increases as the process progresses.

Further Examination of the Solution.—From previous work we might expect the solution to contain either benzoperacid or acetperacid, or both, together with hydroperoxide.

0.6035 gram of pure peroxide was shaken with 50 cc. water at 25° for two and one-half days, the change being complete in this time. The solution was then filtered from the benzoic peroxide, cooled to 15°, and 2 grams acetic anhydride added and dissolved by shaking. The solution was kept cooled to 15° and soon became turbid, owing to the separation of an oil. On scratching the side of the vessel with a glass rod, the oil solidified and separated at the bottom as crystals. After standing for one-half hour the supernatant liquid became perfectly clear, and the addition of more acetic anhydride produced no further separation. The crystalline product was separated from the solution and was found to consist of pure benzoic acetic peroxide. The crude substance melted at 37° to 38°; recrystallized at 38° to 39°. 0.1496 gram required 16.6 cc. N/10 thiosulphate; calculated 16.6 cc. A solution of benzoperacid, treated with acetic anhydride under the same conditions, showed the same formation of benzoic acetic peroxide. The formation of the latter in the hydrolyzed solution is, therefore, accounted for by the presence of benzoperacid.

$$C_6H_5CO.OO.H + (CH_3CO)_2O = C_6H_5CO.OO.COCH_3 + CH_3COOH.$$

The filtrate from the crystalline peroxide was allowed to stand an hour for the hydrolysis of unchanged acetic anhydride, and was then extracted three times with one-third volume of pure ether in order to remove all benzoic acetic peroxide or benzoic acid, and any unchanged benzoic peracid. The ethereal solution was then treated with sodium carbonate solution which was added until, after shaking thoroughly, it remained permanently alkaline.

The ethereal solution, on evaporation, left a small amount

of residue having the very penetrating odor of acetic peroxide. This would indicate the presence of acetperacid in the original solution, were it not true that this solution contained a small amount of hydroperoxide. The alkaline extract was acidified and extracted thoroughly with ether. On evaporation there remained a residue of less than 0.02 gram of benzoic acid. A blank experiment, in which 0.1 gram of benzoic acid was subjected to exactly the same treatment, resulted in its complete recovery. A solution of benzoperacid, on standing, slowly changes to benzoic acid. As the above solution had stood two and one-half days and contained considerable benzoperacid, the presence of the small amount of benzoic acid obtained is easily accounted for, and it may be concluded that the primary hydrolysis of the peroxide results in the formation of no benzoic acid. This experiment also illustrates the ease with which a peracid in aqueous solution may be acetylated, and so completely removed from the acid accompanying it.

Benzoic acetic peroxide, therefore, hydrolyzes according to the following equation:

$$C_6H_5CO.OO.COCH_3 + H_2O = C_6H_5CO.OO.H + CH_3COOH.$$

The possible hydrolysis into acetperacid and benzoic acid is excluded, or extremely minimized by the absence of benzoic acid.

From the three quantitative experiments previously detailed, it can be seen, however, that the total amount of peracid in solution is much in excess of the possible amount of benzoperacid, taking into consideration the amount of benzoic peroxide which has been formed. From this it might be concluded that the solution contains acetperacid. The presence of the latter may be explained by the following reaction:

$$C_6H_5CO.OO.COCH_3 + C_6H_5CO.OO.H = C_6H_5CO.OOCO.C_6H_5 + CH_3CO.OO.H.$$

This would also explain the formation of benzoic peroxide. The formation of the latter might also be explained by the action of benzoperacid on benzoic acid, and this explanation is suggested by the absence of benzoic acid. We have found,

however, that benzoperacid and benzoic acid remain together in solution indefinitely without the formation of a trace of peroxide, which would be recognized by its precipitation.

The following facts leave no doubt as to the accuracy of the explanation given. As already noted, a solution of benzoic acetic peroxide becomes turbid on standing. If a few drops of dilute sulphuric acid be added to the solution this turbidity is prevented. If, besides the acid, a solution of benzoperacid be added, the turbidity appears under exactly the same conditions where, without the peracid, it is prevented. This fact shows that the latter is a factor in the formation of the benzoic peroxide. Furthermore, from the analogy between peroxides and anhydrides which this work has brought out, and from the reactivity of peracids and anhydrides, it might be expected that the former would also react with peroxides. The fact, already noted, that the amount of benzoic peroxide formed increases with the use of less water, is to be attributed to the increased concentration of the benzoperacid.

If a freshly prepared solution of acetic peroxide be treated with a solution of benzoperacid, the solution quickly becomes turbid, owing to the separation of benzoic acetic peroxide. The hydrolyzed solution of acetic peroxide, of course, does not show this behavior.

A drop or so of acetic acid has the same effect in preventing, or at least retarding, the formation of benzoic peroxide. If benzoic acetic peroxide be hydrolyzed in 5 per cent acetic acid, the formation of benzoic peroxide is altogether prevented. Such a solution, after standing three weeks, was evaporated in vacuum. The residue had a penetrating peracid odor and dissolved completely in sodium carbonate. There was, therefore, no benzoic peroxide formed, and none of the original peroxide remained unchanged. From these facts it further appears that the peracid owes its reactivity to its ion rather than to the undissociated molecule.

Hydrolysis of Other Peracids.

The behavior of aqueous solutions of benzoic peracid and phthalic monoperacid was also investigated.

Benzoperacid was prepared by Baeyer by the action of sodium ethylate on benzoic peroxide. As the substance can be preserved only a short time, it is best prepared in small quantities for experimental purposes in the following way: 24 grams of benzoic anhydride were pulverized and added to a solution of 11 grams potassium hydroxide in 250 cc. of 2.6 per cent hydroperoxide, cooled to 0°. After shaking for five minutes, the anhydride had gone into solution and a considerable amount of flocculent benzoic peroxide had been formed. This was removed by filtering through glass wool. The filtrate was then acidified with cold, dilute sulphuric acid and extracted twice with a small quantity of chloroform. On evaporating the solvent a residue of 11 grams remained, of which 2.8 grams were benzoperacid.

The solution, in accord with previous experience, was found to change slowly to hydroperoxide and benzoic acid. The change was followed by comparing the immediate liberation of iodine in dilute acetic acid solution with the total liberation. The change was found to take place much more rapidly in a dilute sulphuric acid solution (1 per cent), which indicates the hydrolytic nature of the process. The solutions were allowed to stand at room temperature. The numbers given in the tables represent cc. of N/10 thiosulphate required by 10 cc. of the solution.

The solution in sulphuric acid was treated with sufficient sodium acetate to neutralize it before estimating the "immediate" iodine.

Time in days.	Immediate.	Total.
0	9.6	9.6
10	8.2	8.7
20	7.2	8.0
30	5.9	6.9
	Acidulated Solution.	
0	9.6	9.6
10	4.9	8.7
20	3.1	8.4
30	1.6	8.1

Both solutions are ultimately changed completely into hy-

droperoxide, as indicated by the action on potassium iodide and the complete loss of odor. Furthermore, on saturating a 10 per cent solution of hydroperoxide with benzoic acid it is impossible to detect the formation of any peracid.

The phthalic monoperacid of Baeyer was found to undergo the same change with much greater rapidity. When in solution one-half of this substance (N/2 in active oxygen) was found to be changed in twenty-four hours. At the end of four days the change was complete.

This investigation was undertaken at the request of Professors Freer and Novy of the University of Michigan, whose article, "The Foundation, Decomposition, and Germicidal Action of Benzoyl Acetyl and Diacetyl Peroxides," has already been referred to. In the article of Freer and Novy are contained certain views concerning the hydrolysis of benzoic acetic peroxide which were held at that time, but which it has been found necessary to modify somewhat.

UNIV. OF MICHIGAN, LABORATORY
OF GENERAL CHEMISTRY.

Contributions from the Sheffield Laboratory of Yale University.

XCIX.—ON THE IODIDES OF CAESIUM.

BY H. W. FOOTE.

The periodides of caesium have been described by Wells[1] and by Wells and Wheeler,[2] who prepared the compounds CsI_3 and CsI_5. The object of the present investigation has been to show, primarily by means of solubility determinations, that these polyiodides and no others exist, at least within the range of temperatures investigated.

If water be brought in contact with an excess of any two caesium iodides, which can exist together, or with one iodide and iodine, the solubility of the mixture will have a certain definite value for any one temperature. This becomes evident by applying the phase rule,

$$v = C + 2 - P,$$

where v represents the number of physical conditions which

[1] Am. J. Sci., **43**, 17 (1892).
[2] *Ibid.*, **44**, 42 (1892).

may be varied, as concentration, pressure, and temperature, C the number of components making up the system, and P the number of phases. There are three components in the system, caesium iodide, iodine, and water, and four phases, consisting of the two iodides, or an iodide and iodine, solution and vapor. Hence,

$$v = 3 + 2 - 4 = 1,$$

or the system is monovariant. If the temperature be fixed, the solubility will adjust itself accordingly. Under working conditions the case is somewhat different theoretically. Here the vapor phase may be disregarded, leaving three phases, and we have

$$v = 3 + 2 - 3 = 2.$$

The system is under constant atmospheric pressure, however, fixing one of the variable conditions, and if the temperature be chosen as the other, the solubility will adjust itself as before. As solubility varies but slightly with great variations in pressure, the solubilities of the iodides under the vapor pressure of the solution or under atmospheric pressure are practically identical. In applying the phase rule below, it will be assumed that the system exists under its own vapor pressure with the vapor phase present.

While the solubility for any temperature is fixed, provided there is an excess of the solid phases, it will change as soon as the solid phases change their composition. Starting, then, at a given temperature from a solution of caesium iodide in water with excess of solid caesium iodide, if enough iodine be added to combine with a part of the caesium iodide to form the first periodide, the solubility will remain constant as long as these two iodides are present in the solid form. By adding enough iodine to combine with all the caesium iodide to form the first periodide and the next higher one, the solubility will be different from the first, but it will remain constant as long as these two iodides are present, without regard to the relative amounts. It will change only when the periodides change in composition. It may be taken as proof that the iodides have not changed in composition if the saturated

solutions remain constant throughout. When the composition of the saturated solution changes, it is proof that at least one solid phase has changed. By properly varying the quantities of iodine and caesium iodide and determining the solubility of each mixture, we can determine the number of different iodides which are capable of existing at any one temperature.

If the solution saturated with two iodides be cooled to the freezing-point, ice will separate. Five phases are then present, ice, the two iodides, solution and vapor, and the system becomes non-variant. Such a system can exist only at its cryohydric temperature, and the composition of the solution is fixed. When the composition of the iodides changes, the cryohydric temperature may change and the composition of the solutions will change. Here, again, we have a means of determining the number of iodides existing.

Caesium triiodide was prepared by treating a hot solution of caesium iodide with about half the calculated quantity of iodine, filtering, and allowing the solution to crystallize. A very beautiful product of the triiodide was obtained in this manner. In carrying out the experiments which have been outlined above, mixtures of caesium iodide and finely powdered iodine, or of caesium triiodide and iodine, were used. The mixture was usually heated for some time with water at as high a temperature as was practicable, and then allowed to cool and crystallize, so that no free iodine should remain in case combination was possible. The mixtures in definite amounts were treated with known quantities of water, so that the composition of the undissolved iodides could be calculated approximately, when the solubility of the mixture in water was found. The proportions of iodine were varied as much as possible. If, for instance, the solubility of a mixture of caesium triiodide and caesium pentaiodide was desired, two or more mixtures were made up in such proportions that the composition of the undissolved residue varied as much as possible between the composition of caesium triiodide and that of caesium pentaiodide. If no intermediate iodide exists, the solubility should be the same no matter what the proportion

of CsI_3 and CsI_5 may be. In case an intermediate iodide is present, as CsI_4, we should expect one value for the solubility when the composition of the residue falls between CsI_3 and CsI_4, and a different value when the composition is between CsI_4 and CsI_5.

Solubility determinations on the mixtures described were carried out usually in test-tubes which were placed in a thermostat. The mixtures were stirred continually for some hours by means of a flattened glass rod, which dipped to the bottom and was kept revolving by means of a turbine attachment. Sometimes the solutions were first prepared at a higher temperature and then placed in the thermostat and stirred. The results were practically the same whichever method was used. When the solutions were saturated, a quantity of the liquid was drawn off directly into a weighed specimen-tube, through a tube provided with a plug of glass wool to act as a filter. At the higher temperatures the tube was first warmed before being dipped in the liquid. The solution was weighed and transferred to a measuring-flask, and aliquot portions used to determine caesium iodide and iodine. The former was determined by evaporating the solution to dryness in a small porcelain dish and heating very slightly over a flame, the latter by titration with sodium thiosulphate.

The solubility determinations at the cryohydric temperatures, and for 35°.6 and 52°.2, are given in Table I. The solubilities are expressed in parts by weight of caesium iodide and iodine in 100 parts by weight of solution. Column (1) represents the solubility of pure caesium iodide; column (2), the solubility of a mixture of caesium iodide and caesium triiodide, *i. e.*, the solubility of a mixture of iodides containing more than 50.58 per cent of caesium iodide in the undissolved residue, this value being the percentage of caesium iodide in CsI_3. Should the solubility change as the percentage of caesium iodide in the undissolved residue changes, it would indicate that one or more intermediate iodides, as CsI_3 exist. The fact that the values obtained are practically constant, although the percentage of caesium iodide was varied largely, shows that no intermediate iodide forms. In the same way,

column (3) represents the solubility of mixtures of CsI_3 and CsI_5, *i. e.*, the solubility of mixtures containing between 50.58 and 33.85 per cent of caesium iodide in the undissolved residue, the latter value being the percentage of caesium iodide in CsI_3. Here, again, although the mixtures varied largely in composition, practically constant results show that intermediate iodides do not exist. Finally, column (4) gives the solubility of mixtures of CsI_5 and I, *i. e.*, of mixtures containing less than 33.85 per cent of CsI in the undissolved residues.

Table I.—Solubility of Caesium Iodides.

	(1)	(2)		(3)		(4)	
	Pure CsI.	CsI and CsI_3.		CsI_3 and CsI_5.		CsI_5 and I.	
Temperature.	CsI.	CsI.	I.	CsI.	I.	CsI.	I.
	Per cent.	Per c't.	Per c't.	Per c't.	Per c't.	Per c't.	Per c't.
Cryohydric	27.73	27.53	0.09	3.14	0.25	0.88	0.35
	27.64	27.51	0.09	3.59	0.35	0.84	0.34
	T = −4°.0	T = −4.°0		2.82	0.35	0.83	0.34
				T = −0°.4		T = −0°.2	
35°.6	51.35	51.49	0.71	10.67	1.75	3.66	1.47
	51.61	51.84	0.71	10.78	1.86	3.82	1.73
52°.2	....	....	...	16.51	4.34	6.45	3.52
				17.06	4.70	6.99	3.13
						6.87	3.29
						6.44	3.61

The fact that the values in the above table are practically constant within the limits mentioned shows that other iodides do not form.

A dilatometer was filled with a mixture of caesium pentaiodide and iodine with a small quantity of water. The increase in volume was noted as the bulb was heated in a large water-bath. A sudden increase in volume was noted at 51°.5, and it was found that the mixture melted, forming a heavy liquid at the bottom of the dilatometer, over which was the aqueous solution. The following two sets of readings were taken to establish this temperature. The first (Table II.) in order to obtain the approximate melting-point, and the second set (Table III.) to fix it accurately:

Table II.

Dilatometer scale.	Temperature.
1.40	25°.1
2.13	29°.9
2.99	34°.85
4.09	40°.4
5.09	45°.1
6.20	49°.9
23.90	52°.7

Table III.

Dilatometer scale.	Temperature.
3.30	50°.9
11.5	51°.6
2.2	51°.4
11.7	51°.6

The true melting-point was therefore taken to be 51°.5. At this temperature there are five phases, iodine, caesium pentaiodide, heavy liquid, aqueous solution and vapor, and three components. The system is thus non-variant and it can exist only at this temperature. Each liquid phase will have a definite composition, whatever the proportions of caesium pentaiodide and iodine. On raising the temperature, one phase will disappear and the system will become monovariant again. Under ordinary conditions, either the caesium pentaiodide or iodine will melt completely when the temperature is raised, depending on which is in excess, and there will be either the monovariant system caesium pentaiodide, heavy liquid, aqueous solution, and vapor, or iodine, heavy liquid, solution and vapor. The composition of the solutions in either system for any one temperature will be fixed irrespective of the relative quantities of each phase, but the solutions in the two systems will not have the same composition.

The composition of the heavy liquid from the mixture of caesium pentaiodide and iodine was determined by means of the apparatus shown in Fig. I. AB is a glass rod ground at B to fit tightly into the large outer tube. The latter is drawn out below and passes through a stopper into a weighed specimen-tube. Through the other hole in the stopper a tube passes as indicated. The mixture of iodine and pentaiodide

with water is placed in the outer tube and the apparatus placed in a thermostat, so that the water comes nearly to the top of the outer tube. The mixture is stirred thoroughly, and when the solution is saturated the rod AB is loosened, and by sucking at C the heavy liquid is drawn through into the specimen-tube and can then be analyzed. A plug of glass wool is placed in the narrow tube opening into the specimen-tube to serve as a filter for the heavy liquid.

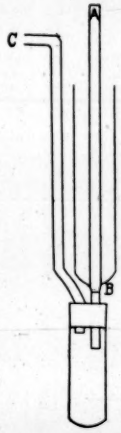


Fig. I.

In Table IV., the solubilities of mixtures of caesium triiodide and pentaiodide, and of the pentaiodide and iodine are given for 52°.2 and 72°.6. The solubilities at 52°.2 are partly taken from Table I. The lower temperature is practically the same as the melting-point of caesium pentaiodide and iodine under water, and it will be noticed that the solubility of the pentaiodide and iodine is the same whether caesium pentaiodide or iodine is present in excess. At 72°.6 the solubility of this mixture depends on which solid phase is present. The same is also true in regard to the composition of the heavy liquid which forms. At the melting-point the composition is fixed. At higher temperatures it depends on which phase is present. The actual percentages of caesium iodide and iodine are given as before. Column (1) shows the composition of solutions saturated with CsI_3 and CsI_5; column (2), the composition of solutions in which CsI_5 is the solid phase; and column (3), the composition of solutions with iodine as the solid phase.

A dilatometer filled with excess of caesium triiodide and pentaiodide, moistened with water, showed no melting-point when heated above 90°.

It was noticed by Wells and Wheeler[1] that various mixtures of caesium pentaiodide and iodine all melted at the same temperature, about 73°. At this temperature there would be

[1] *Loc. cit.*

Table IV.—Solubility of Caesium Iodides.

Temp.	(1) Solid phases = CsI_3 and CsI_5.		(2) Solid phase = CsI_5.				(3) Solid phase = I.			
			Solution.		Heavy liquid.		Solution.		Heavy liquid.	
	CsI.	I.	CsI.	I.	CsI.	I.	CsI.	I.	CsI.	I.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
52°.2	16.51	4.34	6.45	3.52	22.94	73.72	6.87	3.29	22.80	74.63
	17.06	4.70	6.99	3.13	....	....	6.44	3.61	....	....
72°.6	27.03	14.72	16.51	10.86	27.12	68.48	6.40	4.18	17.68	80.02
	26.94	15.43	16.82	10.15	28.01	68.34	6.14	3.98	....	....

four phases present, caesium pentaiodide, iodine, liquid and vapor, and two components, caesium iodide and iodine. The system would, therefore, be non-variant and the composition of the liquid formed at this temperature should be constant, regardless of the proportions of caesium pentaiodide and iodine, provided both be present.

To test this point, mixtures of caesium pentaiodide and iodine were made in various proportions by melting together caesium triiodide and iodine. The mixtures were placed in the bulb A of the tube (Fig. II.), the lower opening being closed with a platinum cone and glass wool to act as a filter. The tube was placed in a bath and heated till the mixture began to melt. By slight suction at B the melted liquid was drawn into the bulb C. The tube was then removed from the bath and the material in C broken out carefully and analyzed. Three determinations were made in this manner. The mixtures were always heated somewhat above the temperature where melting began in order to get liquid enough to analyze. The following results were obtained:

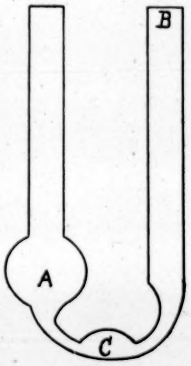


Fig. II.

Table V.

(Caesium pentaiodide contains 33.85 per cent CsI.)

	Percentage CsI in mixture.	Percentage CsI found in liquid.	Temperature at which melting began.	Temperature at which liquid was drawn over.
1	29.96	20.20	73°	77°–78°
2	19.96	18.87	73°	"
3	10.29	18.03	73°.5	79°

The results in the second column agree as well as could be expected and show that the composition of the melted liquid is practically constant. This serves as further proof that iodides higher than CsI_8 do not exist at this temperature, for if a higher iodide did exist it should form a liquid with iodine

having a composition different from that above and with a different freezing-point.

In the preceding article it has been shown, chiefly by means of solubility determinations, that caesium triiodide and caesium pentaiodide are the only periodides of caesium existing between —4° and 73°. The phase rule has served as a guide throughout and the results obtained agree in all cases with the theoretical conclusions.

NEW HAVEN, CONN., Oct., 1902.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF PICRIC ACID.[1]

BY C. LORING JACKSON AND R. B. EARLE.

The following paper contains a description of some new compounds, not of much importance, which were prepared in our work upon the colored addition-compounds formed from sodic alcoholates and nitro derivatives of benzol.

Picryl Bromide (*1-Brom-2,4,6-trinitrobenzol*), $C_6H_2Br(NO_2)_3$. —This substance was prepared in the hope that it would lead to trinitroanisol with less trouble than the common way of making it from picryl chloride. The yield, however, was so small that the method did not prove of value. The process for making trinitroanisol from anisic acid, on the other hand, gave excellent results, and is described in our paper on the colored addition-compounds.

Twenty-five grams of 1-brom-2,4-dinitrobenzol were added to a mixture of 500 cc. of fuming nitric acid, of sp. gr. 1.51, and 200 cc. of fuming sulphuric acid, of sp. gr. 1.86, and the whole boiled vigorously for about three hours in a flask closed with a glass bulb. At the end of this time most of the nitric acid had been driven off, and the liquid ceased to boil quietly, but began to effervesce slightly and to give off very dark red fumes. It was then allowed to cool, poured into a large volume of ice-water, and the precipitate formed dried on a porous plate to get rid of adhering oily impurities. The solid

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science, by R. B. Earle.

was recrystallized from a mixture of alcohol and benzol until it showed the constant melting-point 122° to 123°, when it was dried at 100° and analyzed with the following result:

0.2820 gram substance gave, by the method of Carius, 0.1824 gram argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_3$.	Found.
Br	27.37	27.52

The yield was small, not more than 25 per cent of the theoretical, which we ascribe to oxidation during the long boiling, but, if an attempt was made to check this by diminishing the length of the boiling, little or none of the substance was formed. That it is really the picryl bromide was proved by its conversion into trinitroanisol, melting-point 64°, by treatment with sodic methylate.

Properties of Picryl Bromide.—It crystallizes from alcohol in large, yellowish-white crystals, consisting of long plates terminated at each end by two planes at an acute angle, which is often truncated. Rhombic plates were also observed. Frequently arborescent, frost-like groups occur, with many branches set obliquely to the trunk and each branch bordered with rhombic plates, giving it a jagged outline. It melts at 122° to 123°, and is freely soluble in benzol or acetone; soluble in alcohol, cold or hot, chloroform, ether, methyl alcohol, glacial acetic acid, or carbonic disulphide; slightly soluble in cold, soluble in hot ligroin; insoluble in water. The strong acids do not act upon it even when hot, nor do cold alkalies affect it, but it is easily attacked by hot solutions of an alkali. Sodic methylate converts it into trinitroanisol, as has been already stated. The best solvent for it is a mixture of alcohol and benzol.

Phenyl Picrate, $C_6H_2(NO_2)_3OC_6H_5$.—A solution of sodic phenylate was prepared by dissolving 0.4 gram of sodic hydrate in 1.2 grams of phenol mixed with a little water; 2.6 grams of picryl chloride were then added to this solution in small quantities at a time, stirring the liquid constantly during the addition. The mass soon took on a dark color, and much heat was developed. On washing the product with

water, a dirty, insoluble mass was obtained, which was crystallized from a mixture of alcohol and benzol until it showed the constant melting-point, 153°, when it was dried at 100° and analyzed with the following result:

0.1676 gram substance gave 20.2 cc. N at 20° and 769.3 mm.

	Calculated for $C_6H_2(NO_2)_3OC_6H_5$.	Found.
N	13.77	13.96

Properties of Phenyl Picrate.—It crystallizes from a mixture of alcohol and benzol in yellowish, short, thick prisms, probably of the monoclinic system, which are terminated by two planes at an obtuse angle. It melts at 153° and is freely soluble in benzol or acetone; soluble in methyl or ethyl alcohol, chloroform, or cold glacial acetic acid, freely soluble in the last when hot; slightly soluble in ether; insoluble in water or ligroin. The best solvent for it is a mixture of alcohol and benzol. Willgerodt[1] prepared this substance but gives no description of it.

Action of Acetoacetic Ester on Phenyl Picrate.—In an earlier paper[2] from this laboratory it was shown that the phenoxy groups in dichlordiphenoxyquinone were easily replaced by malonic ester residues, in fact this gave the best method of preparing the dichlorquinonedimalonic ester. The following experiment was tried to see whether the phenoxy group in the phenyl picrate would also be susceptible of replacement: A solution of sodic acetoacetic ester was prepared by adding 0.22 gram of acetoacetic ester to the solution of sodic ethylate from 0.04 gram of sodium and absolute alcohol, and to this was added a benzol solution of 0.5 gram of phenyl picrate. The mixture took on a deep-red color almost immediately, but we do not feel certain whether this was due to the salt of the picrylacetoacetic ester or to the formation of an addition-product (salt of a quinolnitro acid). The mixture was allowed to stand twenty-four hours at ordinary temperature, after which it was washed with water in a separating-funnel and the aqueous washings acidified with dilute hydrochloric

[1] Ber. d. chem. Ges., **12**, 1278 (1879).

[2] This JOURNAL, **17**, 597.

acid. The oily precipitate thus obtained was redissolved in sodic hydrate, filtered and acidified once more. As the precipitate was still gummy, it was extracted with carbonic disulphide, the extract evaporated to dryness, washed with a little cold alcohol, and recrystallized from alcohol until it showed a constant melting-point. As this lay at 97° to 98° there can be no doubt that the substance is the trinitrophenylacetoacetic ester discovered by Dittrich,[1] and that the phenoxy group is easily replaced by the acetoacetic ester residue.

4-Brom-2-nitrophenyl Picrate, $C_6H_2(NO_2)_3OC_6H_3BrNO_2$.—Two grams of the sodium salt of 4-brom-2-nitrophenol were dissolved in 50 cc. of hot alcohol and 2 grams of picryl chloride were added to the solution in small portions at a time, with constant stirring. The heavy, yellow, crystalline precipitate formed was filtered out, washed with water, and recrystallized from acetone, until it showed the constant melting-point, 232°, when it was dried at 100° and analyzed with the following result:

0.2009 gram substance gave, by the method of Carius, 0.0885 gram argentic bromide.

	Calculated for $C_6H_2(NO_2)_3OC_6H_3NO_2Br$.	Found.
Br	18.63	18.75

Properties of 4-Brom-2-nitrophenyl Picrate.—It crystallizes from acetone in short, thick prisms, probably belonging to the monoclinic system, terminated at each end by two planes at an obtuse angle to each other. Its color is yellowish-white, and it melts at 232°. It turns brown on exposure to the air. It is freely soluble in hot acetone, soluble in it when cold; soluble in hot benzol, slightly soluble in cold; slightly soluble in ethyl or methyl alcohol, chloroform, ether, or glacial acetic acid; insoluble in water or ligroin. The best solvent for it is acetone. It seems to form a colored addition-compound with sodic acetoacetic ester, but this may be instead the red salt of picrylacetoacetic ester, as pointed out in the last section.

[1] Ber. d. chem. Ges., **23**, 2720 (1890).

Contributions from the Chemical Laboratory of Harvard University.

ON SYMMETRICAL DINITROBENZOLSULPHONIC ACID.[1]

By C. Loring Jackson and R. B. Earle.

In the course of our work on the colored addition-compounds derived from nitrobenzols and sodic alcoholates (quinolnitro acids) it became desirable to study the behavior of the symmetrical dinitrobenzolsulphonic acid, but on looking up the literature we could find no description of this substance. Limpricht[2] had prepared an acid by the action of nitric and sulphuric acids on metanitrobenzolsulphonic acid, to which this constitution would naturally be assigned, but Sachse,[3] who studied it more fully, determined its structure as $(NO_2)_1,_1,_2,SO_3H_3$.

We therefore prepared the symmetrical dinitrobenzolsulphonic acid from the dinitroaniline obtained from symmetrical trinitrobenzol by decomposing the diazoethylxanthogenate and oxidizing the product. As none of these processes could have produced a molecular transformation, there is no doubt that our acid is the symmetrical dinitrobenzolsulphonic acid. This acid proved itself identical with the acid of Limpricht and Sachse, just mentioned, as appears from the following comparison:

	Our acid.	Limpricht.
Melting-point of chloride	98°–99°	97°
" " amide	234°–235°	235°

Sachse found 89° for the chloride and 238° for the amide. The barium salt from each acid crystallizes with 3 molecules of water, and for greater certainty its solubility was determined with a salt made from our acid and with one from an acid made by the method of Limpricht and Sachse.

One hundred parts of water at 20° contain the following number of parts of the salt free from water of crystallization:

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science, by R. B. Earle.

[2] Ber. d. chem. Ges., 9, 554.

[3] Ann. Chem. (Liebig), 188, 143 (1877).

Our salt.		Sachse's salt.	
4.41	4.39	4.45	4.37

There can be no doubt, therefore, that Sachse made some mistake in his work on the constitution of his acid, since it is evidently the symmetrical and not the vicinal isomer. Sachse's work consisted in reducing the dinitro acid to a diamidobenzolsulphonic acid, replacing each amido group by an atom of bromine by the diazo reaction, and comparing the melting-points of the chloride and amide of this dibrombenzolsulphonic acid with those of the three isomers already known. As they coincided with none of these, it followed that the substance was the only remaining isomer, the as yet undiscovered 1,2-dibrom-3-sulphobenzol. We have followed Sachse's constitutional work as closely as possible, but, unfortunately, the amount of substance at our disposal was too small to give perfectly definite results, and it was too late to prepare more of this acid, which requires heating with nitric acid for fourteen days. The diamidobenzolsulphonic acid obtained by us showed the characteristic crystalline form described by Sachse. The dibrombenzolsulphonic acid was converted into the chloride, but showed no signs of solidifying after standing for a week. It was accordingly converted into the amide, which melted at 203° three times in succession during its recrystallization from alcohol, the residue from the mother-liquors of the last crystallization melted at 202° to 203°, and there was not enough substance left for another crystallization. We compare below the melting-points given by Sachse, those of the chloride and amide of the 1,3-dibrom-5-sulphobenzol determined by Lenz,[1] and our result:

	Sachse.	Lenz.	Our result.
Chloride	127°	57°.5	....
Amide	215°	203°	203°

While it is improbable that a chloride melting at 127° would remain obstinately liquid, as ours did, this behavior would be expected in summer from a chloride melting at 57°. On the other hand, a determination of the solubility of our amide did not agree with that given by Lenz, as he found

[1] Ann. Chem. (Liebig), 120, 158.

0.0958 gram of the substance in 100 grams of solution at 18°, while we found 0.0061 and 0.0060. The probable reason for this discrepancy is that he allowed his amide to stand with the water eleven days, when partial decomposition might have taken place, while our determination was carried through in two hours. Our experimental results then do not settle finally the dibrombenzolsulphonic acid made from Sachse's dinitrobenzolsulphonic acid, but they make it highly probable that it is identical with Lenz's 1,3-dibrom-5-sulphobenzol. Fortunately, however, this experimental proof is unnecessary, since our preparation of the dinitrobenzolsulphonic acid from symmetrical dinitroaniline has proved that its structure is $(NO_2)_2 1,3,SO_3H5$, and, therefore, that Sachse's dibrom acid is identical with that of Lenz in spite of Sachse's different melting-points. How Sachse made this mistake in the melting-points of his chloride and amide we are unable to explain, especially as his paper gives evidence of very careful work. They fall near those of the 1,2,3-tribrom-5-sulphobenzol derivatives[1] (Sachse: 127° tribrom, 127° for the chloride, 215° and 210° for the amide), but that Sachse had these tribrom compounds in hand is disproved by his numerous analyses of the salts of the acid.

The result of our work is that the dinitrobenzolsulphonic acid of Limpricht and Sachse is the symmetrical isomer, $(NO_2)_2 1,3,SO_3H5$, and therefore the vicinal acid $(NO_2)_2 1,2,SO_3H3$ still remains to be discovered.

EXPERIMENTAL PART.

Preparation of 1,3-Dinitro-5-sulphobenzol, $C_6H_3(NO_2)_2SO_3H$, from Symmetrical Dinitroaniline.

Ten grams of 1,3,5-dinitroaniline (made from trinitrobenzol[2]) were dissolved in hot hydrochloric acid (one part of strong acid to one of water). The solution was filtered hot, allowed to cool, and treated with 14 grams of sodic nitrite (a large excess over the amount needed by the theory), which was added in small portions at a time, the flask being cooled by running water after each addition. The solution soon became

[1] Lenz: Ann. Chem. (Liebig), 181, 29.
[2] Bader: Ber. d. chem. Ges., 24, 1654 (1891).

filled with a dirty, brownish-red precipitate of the diazo chloride. As soon as all the nitrite had been put in, the liquid was diluted to 300 cc. with cold water, and a fresh solution of 15 grams of potassic ethylxanthogenate[1] in 100 cc. of cold water was added in small portions at a time, with constant shaking. During this addition the solution turned yellow, and a bright yellow precipitate of the diazoxanthogenic ester was formed, which floated on the surface. On warming the mixture to 80° the yellow solid was converted into a heavy brown oil, and nitrogen was given off. This oil was extracted with ether, and, after distilling off the ether on the water-bath, it was oxidized directly without any attempt at purification, or even saponification. For this oxidation nitric acid was used, beginning with a mixture of one part of strong acid with one of water to avoid too violent action. It was boiled with this diluted acid until it ceased to act with it, after which enough strong nitric acid was added to the boiling solution to start the oxidation once more, and this treatment was repeated until all the oil had dissolved and no more red fumes were evolved. The solution thus obtained was evaporated on the water-bath until the odor of nitric acid had gone, diluted with water, filtered, and the filtrate digested with baric carbonate until neutral. The tarry phenol, insoluble in water, was present in such small quantity that no attempt was made to identify it. The neutral barium salt was filtered off, and the washings of the insoluble barium salts having been added, the whole was evaporated to dryness on the steam-bath. For purification it was converted into the chloride, which will therefore be described next.

1,3-Dinitrobenzol-5-sulphochloride, $C_6H_3(NO_2)_2SO_2Cl$.—The crude barium salt prepared in the manner just described, after it had been dried on the steam-bath, was mixed in a test-tube with an equal weight of phosphoric pentachloride, and the mixture heated to 150°. At about 140° the reaction began. After it had ended, most of the phosphoric oxychloride was distilled off and the residue treated with cold water. The insoluble part was filtered out, dried *in vacuo*, and purified by dissolv-

[1] R. Leuckart: J. prakt. Chem., [2], 41, 197 (1890).

ing it in chloroform, adding enough ligroin for precipitation, and allowing the mixture to stand, when the turbid solution gradually deposited large, yellowish crystals. These were freed from some tarry matter by washing with cold ether, after which the crystallization from chloroform and ligroin was continued until it showed the constant melting-point, 98° to 99°, when it was dried *in vacuo* and analyzed with the following result:

0.3245 gram substance gave, by the method of Carius, 0.1770 gram AgCl and 0.2788 gram $BaSO_4$.

	Calculated for $C_6H_3(NO_2)_2SO_2Cl$.	Found.
Cl	13.32	13.49
S	12.00	11.80

Properties of the 1,3-Dinitrobenzol-5-sulphochloride.—It crystallizes from chloroform and ligroin in good-sized, yellowish-white, flat prisms, apparently monoclinic or triclinic, the terminations being made up of two principal planes at an obtuse angle to each other, and forming oblique angles with the basal planes. They seem to be arranged in pairs diagonally across the prism. Usually the terminations are much modified, and occasionally develop lancet-shaped ends. As they grow larger they generally become much distorted. It melts at 98° to 99°, and is freely soluble in benzol, chloroform, or glacial acetic acid; soluble in ether; insoluble in water or ligroin. The best solvent for it is a mixture of chloroform and ligroin. It is comparatively stable in contact with hot water, but is decomposed by long boiling with it. Hot alcohol decomposes it rapidly, after it has dissolved it. Hot solutions of the alkalies decompose it very quickly.

1,3-Dinitrobenzol-5-sulphamide, $C_6H_3(NO_2)_2SO_2NH_2$.—This substance was prepared by treating the chloride with a small amount of strong ammonic hydrate and allowing the mixture to stand for a short time, after which it was diluted and the amide filtered off. It was purified by dissolving it in alcohol, adding an equal volume of hot water, and allowing it to crystallize out as the mixture cooled. The melting-point became constant at 234° to 235°. It forms short, slender prisms of a

yellowish color, and is soluble in hot alcohol; soluble in hot water, practically insoluble in cold, yet it is more convenient to crystallize it from a mixture of hot alcohol and water than from water alone; slightly soluble in ether, benzol, chloroform, glacial acetic acid, or ligroin.

Baric 1,3-Dinitrobenzol-5-sulphonate, $(C_6H_3(NO_2)_2SO_3)_2Ba.3H_2O$.—The pure sulphochloride was boiled with water until the whole had dissolved, and the solution evaporated to dryness on the steam-bath, when the free acid separated in large, white crystals, contaminated with a dark-colored impurity. This acid was heated for two hours on the steam-bath to remove the last traces of hydrochloric acid, then dissolved in water, and treated with baric carbonate. The barium salt freed from the excess of carbonate by filtration, was evaporated until it began to crystallize, and purified by several recrystallizations from water. It was dried in the air and analyzed with the following result:

0.4392 gram air-dried salt lost, when heated to 120°, 0.0356 gram H_2O.

	Calculated for $(C_6H_3(NO_2)_2SO_3)_2Ba.3H_2O$.	Found.
H_2O	7.88	8.11

0.2496 gram salt, dried at 120°, gave 0.0912 gram $BaSO_4$.

	Calculated for $(C_6H_3(NO_2)_2SO_3)_2Ba$.	Found.
Ba	21.71	21.48

Properties of the Barium Salt.—It crystallizes from water in masses of pale-yellow prisms, which lose part of their water of crystallization over sulphuric acid, and nearly all of it at 100°, but the last portions are given off very slowly at this temperature, so that it is wiser to heat to at least 120° in drying the salt. It is soluble in alcohol. Its solubility in water was determined as follows:

I. 8.9006 grams solution, at 20°, contained 0.3922 gram salt dried at 140°.

II. 11.0533 grams solution, at 20°, contained 0.4851 gram salt dried at 140°.

100 parts of the solution, at 20°, contained, therefore, the following numbers of parts of the anhydrous salt:

I.	II.
4.41	4.39

The substance forms, with sodic methylate, a salmon-colored salt of a quinolnitro acid,

$$(C_6H_3(NO_2)_2SO_2NaOCH_3)_2Ba,$$

which has been described in another paper. When moistened with benzol, chloroform, or ligroin, it takes on a deep-red color. It is a decidedly stable substance for one of this class.

Preparation of Dinitrobenzolsulphonic Acid from Metanitrobenzolsulphonic Acid According to Sachse.[1]

This work was undertaken in order to make a more careful comparison of this acid with the one prepared by us, because the melting-points of the chlorides and amides pointed to the identity of the two. The process was carried on as follows: Fifty grams of the metanitrobenzolsulphonic acid were boiled for fourteen days with a mixture of 300 cc. of fuming sulphuric acid, of 1.86 sp. gr., and 300 cc. of nitric acid, of 1.50 sp. gr., in a flask provided with a long air-condenser ground into its neck. At the end of this time the mixture was allowed to cool, poured into a large volume of water, and heated in a dish over the water-bath for four days to get rid of the nitric acid, more water being added from time to time to replace that which evaporated. The solution was then treated with an excess of baric carbonate (omitting the treatment with lime used by Sachse), and the barium salt evaporated to crystallization, the first crystals being rejected. The red crystals, which separated from this crude solution, were recrystallized from hot water, when they lost this red color and became yellow, thus removing one of the differences between our acid and that described by Sachse. The crystalline form of this barium salt was also similar to that of ours. To be certain that it was Sachse's salt, it was analyzed with the following result:

0.2983 gram salt, dried at 120°, gave 0.1097 gram of $BaSO_4$.

	Calculated for $(C_6H_3(NO_2)_2SO_2)_2Ba$.	Found.
Ba	21.71	21.63

[1] Ann. Chem. (Liebig), 188, 143 (1877).

The determination of its solubility gave the following results:

I. 6.9690 grams solution, at 20°, contained 0.3098 gram salt dried at 140°.

II. 10.9542 grams solution, at 20°, contained 0.4790 gram salt dried at 140°.

100 parts of the solution, at 20°, contained, therefore, the following numbers of parts of the anhydrous salt:

I.	II.
4.45	4.37

These results prove that the two acids are identical.

Conversion of Sachse's Dinitrobenzolsulphonic Acid into Dibrombenzolsulphonic Acid.

In this part of the work, Sachse's method[1] for determining the constitution of his acid was followed. The reduction of the dinitro to the diamido acid was carried on with sulphuretted hydrogen. For this purpose the ammonium salt (prepared by the action of ammonic carbonate on the barium salt described in the preceding section) was dissolved in 200 cc. of water, mixed with 20 cc. of ammonic hydrate of the common laboratory strength, and treated with sulphuretted hydrogen for two hours. The liquid became hot, turned dark-brown, and deposited a large amount of sulphur. After boiling it to collect the sulphur in larger grains, it was filtered, concentrated, and while hot acidified with acetic acid. After standing for twenty-four hours, large, well-formed, yellowish-red crystals separated, which accord with Sachse's description of the diamidobenzolsulphonic acid, except that we should describe it as soluble rather than difficultly soluble in water. The amount of these crystals was small, and to obtain most of the diamidobenzolsulphonic acid we added an excess of strong hydrochloric acid to the mother-liquor, which threw down a heavy crystalline precipitate of the chloride, since this is but slightly soluble in strong hydrochloric acid. After one recrystallization from water the chloride was converted into the free acid by cautious addition of argentic carbonate, and this

[1] Ann. Chem. (Liebig), **188**, 148 (1877).

changed into the bromide with hydrobromic acid. The bromide, which is more soluble than the chloride, was recrystallized several times from water, but, as this failed to decolorize it completely, we proceeded to the conversion of it into the dibrombenzolsulphonic acid.

The acid, or its bromide, was suspended in freshly distilled hydrobromic acid, and treated for half an hour with a stream of nitrous anhydride (from arsenious anhydride and nitric acid). The liquid was then warmed until the evolution of nitrogen had begun, and after the reaction had spent its violence, heated to boiling. This treatment was repeated until no more nitrogen was given off. The hydrobromic acid was then driven off by warming on the steam-bath, water added, and the barium salt formed with baric carbonate, the solution being filtered hot. The highly colored product was decomposed with sulphuric acid and then again converted into the barium salt, which removed part of the colored impurity, leaving the salt of a light-brown color. The method is essentially the same as that of Sachse.

The baric dibrombenzolsulphonate was converted into the chloride by heating it in a test-tube with a large excess of phosphoric pentachloride (about equal weights of the two substances). The action began at about 100°, but the temperature was carried to 150° to finish the reaction. After most of the phosphoric oxychloride had been distilled off, the cool mass was treated with ice-water, which left the chloride as a brown oil, which did not solidify, even after long standing. Accordingly it was converted into the amide by ammonic hydrate in the cold, and this amide was recrystallized from alcohol. Unfortunately, the amount of material at our disposal was not sufficient to get an absolutely constant melting-point, but that we had nearly approached this point is shown by the following observations made after the last three crystallizations:

Melting-point of crystals.	Melting-point of evaporated mother-liquor.
203°	197°–201°
203°	200°–202°
203°	202°–203°

One more crystallization would undoubtedly have given a constant melting-point, but we did not have the material for it. Sachse[1] found the melting-point 215° for his amide made in precisely the same way. The melting-point of 1,3-dibrombenzol-5-sulphamide is 203° according to Lenz.[2] In the hope of establishing the identity of Lenz's and our amides we determined the solubility of our amide as follows:

I. 87.5 grams solution, at 18°, contained 0.0053 gram substance.

II. 100 grams solution, at 18°, contained 0.0060 gram substance.

100 parts solution, at 18°, contain the following numbers of parts of the amide:

I.	II.
0.0061	0.0060

These results do not agree with the solubility determined by Lenz, which he puts at 0.0958. The difference is undoubtedly due to the fact that Lenz made his solution by soaking the amide for eleven days, during which time partial conversion into the ammonium salt is possible, whereas our solution was made in two hours. The subject is of too slight importance to make it worth while to undertake the work necessary to settle the point by more definite experimental results.

Contribution from the North Carolina Experiment Station.

STUDIES IN NITRIFICATION.

By G. S. Fraps.

This article falls naturally into three parts, as follows:

Part I.—Variations in the nitrifying power of the same soil.

Part II.—The nature of the nitrifying organisms.

Part III.—Determination of the comparative nitrifying power of soils.

[1] Ann. Chem. (Liebig), **188**, 155 (1877).
[2] *Ibid.*, **120**, 158.

PART I.

Variations in the Nitrifying Power of the Same Soil.

This portion of the study was undertaken primarily on account of serious irregularities observed in the nitrifying power of the same soil at different times during the course of work on other portions of this research. For example, a soil taken from a wheat field, May 28, nitrified 143 milligrams nitrogen per kilogram of soil in three weeks, while a second sample, taken three weeks later, nitrified only 20 milligrams under the same conditions.

The two ways in which the nitrifying power of a soil may be studied are as follows :

1. *The Rate of Nitrification in the Soil.*—The quantity of nitrates in the soil may be determined at the end of different periods of time, when the quantity formed per unit of time during each period is a measure of the rate of nitrification in the soil, or its energy of nitrification, as it will be called in this article. The initial energy of nitrification of a soil is measured by its rate of nitrification during the first period.

2. *The Inoculation Energy of the Soil.*—This is taken to mean the power of a soil to bring about nitrification in a sterilized soil which has been placed under proper conditions for nitrification. The measure of the nitrification energy of a given soil is the quantity of nitrates formed in a standard sterilized soil under standard conditions, and in a definite time.

As will be seen later, the nitrification energy of a soil and its inoculation energy are quite different.

The nitrifying power of a soil, meaning both its energy of nitrification and its inoculation energy, depends upon two factors, the number of nitrifying bacteria present and their activity.

The maximum number of nitrifying bacteria which may be contained in a soil, under field conditions, depends upon the nature of the soil itself, since some soils offer a much more favorable medium for the growth of the nitrifying organisms than others. This aspect of the question will be treated in

Part III. It also depends upon the nature and amount of crop residues, nitrogenous fertilizers, humus, and other nitrifiable matters which may be present. With decrease in the amount of food present, or its availability, it is obvious that the soil, aside from its nature, offers a much less favorable medium for the reproduction of the nitrifying bacteria.

The number of nitrifying bacteria in any given soil at any time will depend as much upon the conditions to which the soil is subjected as on its nature. According as favorable or unfavorable conditions prevail, the number of organisms in the soil will be greater or less. Cold, dryness of the soil, and excess of moisture will diminish their numbers, while warmth and a proper amount of moisture will be favorable to their increase. Evidently, the number of nitrifying organisms in any soil is subject to fluctuations, according to the season, and the weather to which it is exposed, and consequently we may expect to find that the nitrifying power of the soil is also subject to variations.

The activity of the nitrifying organisms also varies from time to time. If the rate of nitrification of ammonium sulphate or cottonseed meal is studied under uniform conditions of temperature and moisture, it is seen that the nitrification takes place in stages, a period of activity being preceded and followed by periods of inactivity. That is to say, the rate of nitrification is periodic. A study of the inoculation energy of soils also gives evidence of variations in the activity of the nitrifying organisms.

Variations in Energy of Nitrification.

The rate of nitrification of cottonseed meal and of ammonium sulphate was determined in a number of samples of soil, the measure being the quantity of nitrates formed per week during the first three weeks, and succeeding weeks. The method of work will be described later.

The curves in Fig. I. exhibit graphically the variations in the energy of nitrification with time. The curves were chosen to show how the period of greatest energy of nitrification may come during the first three weeks, the fourth week,

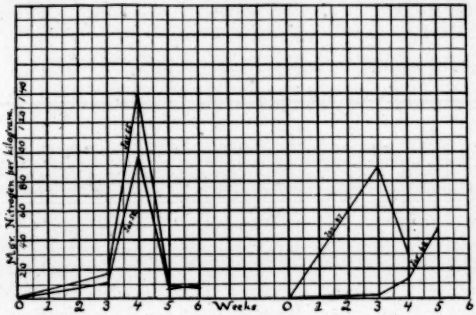


Fig. I.—Rate of nitrification of ammonium sulphate and cottonseed meal.

or the fifth week, according to the condition of the soil at the time of starting the experiment. The results of all the determinations are given in Table I.

Table I.—Energy of Nitrification.

Soil and nutrient.		Milligrams nitrogen per kilogram soil oxidized per week. Three weeks.	Fourth week.	Fifth week.	Sixth week.	Total.
Soil 1748	Inoculation tests					
Jar 55	Cottonseed meal	17	141	9	8	210
" 56	Ammonium sulphate	5	59	..	37[1]	138
" 57	Cottonseed meal	12	109	−57[2]	5	91
" 58	Ammonium sulphate	11	96	6	9	143
Soil 1764	Inoculation tests					
Jar 67	Cottonseed meal	2	94	34	..	133
" 68	Ammonium sulphate	2	53	18	..	69
Soil 1766	Inoculation tests					
Jar 72	Cottonseed meal	10	106	0	..	135
" 74	Ammonium sulphate	2	61	−9[2]	..	57
Soil 1772	Direct nitrification					
Jar 77	Cottonseed meal	2	63	..	..	70
" 79	Ammonium sulphate	1	1	0	..	4
Soil 1772	Inoculation tests					
Jar 81	Cottonseed meal	7	103	..	..	124
" 83	Ammonium sulphate	3	62	..	..	70

[1] Mean of fifth and sixth week.
[2] Dentrification took place.

Soil and nutrient.		Milligrams nitrogen per kilogram soil oxidized per week. Three weeks.	Fourth week.	Fifth week.	Sixth week.	Total.
Soil 1781	Inoculation tests					
Jar 91	Cottonseed meal	31	66	..	..	159
" 93	Ammonium sulphate	25	49	..	..	124
Soil 1781	Direct nitrification					
Jar 87	Cottonseed meal	90	30	..	..	300
" 90	Ammonium sulphate	93	39	3	..	319
Soil 1746	Direct nitrification					
Jar 47	Cottonseed meal	12	..	69[1]	42	218
" 49	Ammonium sulphate	7	..	28[1]	52	129
Soil 1768	Inoculation tests					
Jar 62	Cottonseed meal	1	13	67	..	83
" 65	Ammonium sulphate	2	9	64	..	79

The following statements appear justified by the figures given in the table:

1. The initial energy of nitrification is low in some cases (soils 1766, 1772) and high in others (soil 1781).

2. The rate of nitrification is periodic, reaching a maximum, and then decreasing. The decrease is not due to lack of nitrogen to nitrify, for the soil contains 0.532 gram of nitrifiable nitrogen per kilogram, and the total amount nitrified is less than half of this in most cases.

3. In a given soil, the period of greatest energy of nitrification comes at the same time, whether the nitrogen is supplied in the form of cottonseed meal or ammonium sulphate.

4. The period of greatest energy of nitrification has come, as a rule, in the fourth week. This is the case with six of the nine sets of soils in the table. In one set it came in the fifth week, in one set during the first three weeks, and one during either the fourth or fifth week.

Cause of the Variations.

The explanation of the variations in the rate of nitrification in soils is probably to be found in the life history of the organisms. There seems to be a period during which the germs multiply, and little nitrification takes place, then a short period of rapid nitrification, followed by a period of multiplication with little nitrification. How long a period of

[1] Mean of fourth and fifth week.

time it requires for the organisms to complete this cycle of changes cannot be stated. The maximum time required in any of the experiments here given for the maximum of activity of nitrification to occur was five weeks.

The life activity of the bacteria which assimilate nitrogen on the roots of legumes is also periodic. Cultivated outside of the plant, they assimilate nitrogen with difficulty, only 7 milligrams per gram of sugar consumed by them. When growing in nodules on legumes, according to Nobbe and Hiltner, they are purely parasites, until the bacteria are transformed into bacterioid forms, and then the plant begins to receive the benefit of the nitrogen assimilated by them. The life history of the nitrogen-assimilating bacteria appears parallel to that of the nitrifying organisms; there is a period of multiplication with little assimilation, followed by a period in which nitrogen appears to be assimilated rapidly.

Variations in Inoculation Energy.

A study of the change in the power of soils to induce nitrification in a sterile soil was made at the same time as the determination of its rate of nitrification. The quantity of nitrates formed in three weeks in the sterilized soil kept under standard conditions has been taken as the measure of the inoculation energy of the soils.

The method used was as follows: Four jars of soil were kept under standard conditions, and nitrates determined in samples taken at the end of three, four, five, and six weeks, respectively. At the end of three weeks samples were used to inoculate a sterilized soil. At the end of four and five weeks similar sets were started. The amounts of nitrates formed in these soils in three weeks represents, therefore, the inoculation energy of the four jars of soil at different periods of time.

The inoculation energy of the soils increased rapidly with time. The results of the experiments are contained in Table II., which gives the total quantity of nitrates formed at the end of each period, as well as the inoculation energy of the soil measured as stated.

Table II.—Variation of Inoculation Energy with Time.

Nutrient.	Milligrams nitrogen per kilogram soil. Three weeks. In soil.	Three weeks. Inoculation energy.	Four weeks. In soil.	Four weeks. Inoculation energy.	Five weeks. In soil.	Five weeks. Inoculation energy.
Derived from 1748						
Jar 55 Cottonseed meal	52	81	193	141	202	205
" 56 Ammonium sulphate	15	4	63	57	...	219
" 57 Cottonseed meal	35	12	144	158	86	97
" 58 Ammonium sulphate	32	25	128	147	133	153
Derived from 1781						
Jar 91 Cottonseed meal	93	115	159	123		
" 92 " "	113	99	171	131		
" 93 Ammonium sulphate	75	60	124	75		
" 94 " "	24	75	138	139		

The broken curves in Fig. II. represent graphically the change in the inoculation energy of the soil with time. It might be expected that the inoculation energy of a soil would be related to its nitrification energy, but such does not seem to be the case, as may be readily seen by comparing the curves in Fig. I. with those in Fig. II. for the same soil.

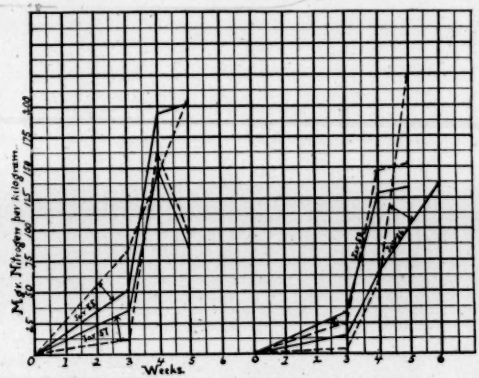


Fig. II.—Inoculation energy of soils (dotted lines) and total nitrification in same soils (solid lines). Arrows link corresponding curves.

There is, however, a close relation between the inoculation energy of the soil and the total quantity of nitrogen oxidized in it. Indeed, after the first three weeks, the inoculation energy of a soil seems to be as great as, or greater than, the total amount of nitrification in it. That is to say, after the first three weeks as much nitrification takes place in the inoculated soil in three weeks as takes place in the soil used for the inoculation in four or five weeks, as the case may be. The change in the power of the soil to induce nitrification is very great.

The relation between the total amount of nitrates formed in the soil and its inoculation energy is shown very clearly in Fig. II., in which the solid lines represent the total nitrification in the soil. Corresponding curves are linked by arrows. Even in the case in which denitrification took place (Jar 57), the inoculation energy of the soil is closely parallel to its total nitrification.

Causes of Variations in Inoculation Energy.

The changes in inoculation energy, as described above, are probably due to an increase in the number of the nitrifying bacteria in the soil. The increase does not seem to be attended with increased energy of nitrification, as has already been shown. That is to say, in the soils which have been studied, which are provided with an abundance of food and kept under favorable conditions, the number of the nitrifying organisms seems to increase throughout the course of the experiment while they nitrify slowly at first, then very rapidly, then very slowly again, in spite of the increase in their numbers.

It is possible that the increase observed in the inoculation energy of the soils is also due, in part, to an increased activity of the organisms, either that they multiply more rapidly in the inoculated soil or they grow in power to nitrify. A change of this kind would be analogous to the increase in activity or "virulence" observed with the bacteria which assimilate nitrogen.

Method of Work.

The following is the method of work followed throughout

this investigation. Two kinds of nitrification tests were made: In the direct nitrification tests, the soil was used as it came from the field; in the inoculation tests, a sterilized soil was inoculated with active soils.

Direct Nitrification Experiments.—The soil was sifted through a 5 mm. sieve and 500 grams of it placed in a porcelain dish and mixed thoroughly with calcium carbonate, cottonseed meal or ammonium sulphate, and water. The mixture was transferred to a pint precipitating jar or fruit jar, weighed, and placed in a large water-bath in a dark closet, kept as nearly as possible at 35°. Every Monday and Thursday each jar was weighed and sufficient water added to restore its former weight. At the end of the period, usually three weeks, the proper amount of water was added to the jar, its contents mixed thoroughly in a porcelain dish, and the nitrates in 100 grams determined by the Tiemann-Schulze method. The remainder of the soil was allowed to nitrify further, if desired.

The amount of ammonium sulphate or cottonseed meal which was used for 500 grams soil contained 0.3 gram nitrogen. The ammonium sulphate was added in solution, after the calcium carbonate and water had been mixed with the soil. The calcium carbonate and cottonseed meal were always mixed thoroughly with the soil before any water was added. The calcium carbonate (2.14 grams) was just sufficient to neutralize all nitric and sulphuric acids which would be formed if all the ammonium sulphate were oxidized. In no case did this occur.

Water was used in quantity sufficient to bring the water content of the soil to one-third of its saturation capacity, allowing for the water already in the soil, and that to be added with the ammonium sulphate (20 cc.), if any. The method used to determine the water saturation capacity of the soils is as follows:

Fifty grams soil were placed on a porcelain plate in a carbon filter and the whole weighed. Water was added in quantity a little more than necessary to saturate the soil, so that a few drops came through, and the tube was allowed to drain, a

cork being placed loosely in it to prevent evaporation. After two hours, the stem of the tube was dried and the whole weighed. Allowance was made for water already in the soil.

Inoculation Experiments.—These differ from the preceding only in the use of a sterilized soil, and its inoculation with the soil to be tested. The same sterilized soil was used in all the inoculation experiments, being a sandy clay soil which had been in the laboratory, in a dry condition, for three years. No attempt was made to sterilize the soil completely, for sterilization as regards nitrifying organisms was all that was desired. A thorough drying is sufficient to accomplish this, but the soil used was also treated with chloroform, and then heated to a moderate temperature in an air-bath.

In case cottonseed meal was used, 20 grams of the soil to be tested were mixed with calcium carbonate and cottonseed meal, and then with 500 grams of the sterilized soil. Water was added in sufficient quantity (one-third of the soil's saturation capacity) and the whole thoroughly mixed. The nitrification was conducted as described above.

If ammonium sulphate was used, 20 grams of the soil were mixed with calcium carbonate and then with the sterilized soil. Water was added, and finally the ammonium sulphate in solution. This order was followed because it was not considered advisable to allow the strong solution of ammonium sulphate to come in direct contact with the germs in the inoculating soil.

It must be noted that the 100 grams of soil taken for the determination of nitrates did not represent one-fifth of the mixture, since the jar contained 500 grams of soil plus water, calcium carbonate, etc. Due allowance has been made for this fact where necessary.

Description of Soils.

1746. Sandy clay soil from a wheat field on the College farm. Little humus. Saturation capacity, 33 per cent.

1746*a*. A second sample, taken three weeks later.

1747. Sandy clay soil, sterilized as described previously. Used in all inoculation experiments. Saturation capacity, 34.3 per cent.

1748. Dark loam from peach orchard on the Experiment Station farm. Contains humus. Saturation capacity, 34 per cent.

1764. Black sandy soil from the Florida Experiment Station. It contained only 0.5 per cent of water when it arrived, and had little nitrifying power.

1764*a*. A second sample, which had been kept in a well-closed fruit jar since the summer of 1901. It was still quite moist.

1766. Loam from a flower bed on the College lawn. Contains much humus.

1766*a*. A second sample, taken three weeks later.

1768. A garden soil.

1772. Sandy soil from the test farm of the North Carolina Department of Agriculture, at Tarboro. Contained only 1.85 per cent water when received, but appeared moist. Saturation capacity, 27.3 per cent.

1779. Poor, light, sandy soil from the College farm. No humus. Saturation capacity, 27.3 per cent.

1779. Rich, dark, sandy soil from the College farm. Contains much humus. Saturation capacity, 46 per cent.

1781. Black sandy soil from the garden of the State Chemist, B. W. Kilgore. Contains much humus. Saturation capacity, 42.5 per cent.

Acknowledgment is hereby made to Chemist H. K. Miller, of Florida, and State Chemist B. W. Kilgore, of North Carolina, for kindness in furnishing samples of soil.

PART II.

The Nature of the Nitrifying Organisms.

In previous articles[1] from this Station by W. A. Withers and the author, the fact was brought out that some soils nitrify cottonseed meal to a greater extent than ammonium sulphate in three weeks, while with other soils the reverse is the case. The explanation advanced in the articles referred to for this circumstance is that the difference is due to the combined influence of three factors :

[1] J. Am. Chem. Soc., **23**, 318 (1901) ; **24**, 528 (1902).

1. Ammonium sulphate may hinder the action of the nitrifying organisms.

2. The acids produced by their life-activity are detrimental to them unless neutralized.

3. There are organisms which convert organic matter directly to nitrites or nitrates, as well as those which oxidize ammonium salts to nitrites.

According to this hypothesis, there are four groups of organisms which take part in the process of nitrification.

Group I. converts organic matter to ammonium salts.

Group II. converts ammonium salts to nitrites.

Group III. converts nitrites to nitrates.

Group IV. converts organic matter to nitrites or nitrates.

As stated, this hypothesis is based on the fact that some salts nitrify ammonium sulphate more readily than cottonseed meal, while other soils nitrify cottonseed meal more readily than ammonium sulphate. The work to be described in this section was designed to test this hypothesis more thoroughly.

The results of the work are as follows:

A. The difference in the ratio of nitrification of cottonseed meal and ammonium sulphate in different soils, is due to differences in the nitrifying organisms contained in those soils.

The following is the evidence in support of this statement:

1. A sterilized soil inoculated with different nitrifying soils nitrifies cottonseed meal and ammonium sulphate in different ratios. The only difference in the conditions of these experiments was the different soils used for the inoculation.

The figures are given in Table III.

Table III.—Relative Amounts of Cottonseed Meal and Ammonium Sulphate Nitrified in an Inoculated Soil.

		Milligrams nitrogen per kilogram soil.		
	Soil.	Cottonseed meal.	Ammonium sulphate.	Ratio.
1748	Loam	73	66	1 : 0.9
1746*a*	Sandy clay	100	53	1 : 0.5
1764*a*	Black sandy soil	99	61	1 : 0.6
1776*a*	Loam	29	7	1 : 0.3
1772	Sandy soil	23	10	1 : 0.4
1781	Black sandy soil	100	84	1 : 0.8

2. The ratio between the amounts of cottonseed meal and ammonium sulphate nitrified is nearly the same in any soil and in the inoculated soil prepared from it (Table IV.).

Table IV.—Relative Amounts of Cottonseed Meal and Ammonium Sulphate Nitrified in a Soil and in Its Inoculation.

		Milligrams nitrogen per kilogram soil.		
	Soil.	Cottonseed meal.	Ammonium sulphate.	Ratio.
1748	Direct	212	176	1 : 0.8
	Inoculation	73	66	1 : 0.9
1746*a*	Direct	176	77	1 : 0.45
	Inoculation	100	53	1 : 0.53
1772	Direct	5	3	1 : 0.6
	Inoculation	23	10	1 : 0.4
1781	Direct	284	267	1 : 0.9
	Inoculation	100	84	1 : 0.8

B. There are two groups of nitrifying organisms in the soil, one of which nitrifies cottonseed meal, the other ammonium sulphate. Besides the evidence afforded by the figures above given in support of this statement, it has been possible to increase the power of a soil to nitrify cottonseed meal, and to diminish it. If the nitrifying organisms are cultivated in a soil containing ammonium sulphate, and used to inoculate other soils, it will be found that their power of nitrifying cottonseed meal has diminished, and in the same way it is possible to increase the power of the soil to nitrify cottonseed meal by cultivation. The results of two sets of experiments of this kind are given in Table V.

Table V.—Effect of the Cultivation of the Organism on the Relative Amounts of Cottonseed Meal and Ammonium Sulphate Nitrified.

	Milligrams nitrogen per kilogram soil.		
Set I. (1746)	Cottonseed meal.	Ammonium sulphate.	Ratio.
Grown in cottonseed meal (mean)	233	162	1 : 0.7
" " ammonium sulphate	190	200	1 : 1.05
Set II. (1772)			
Grown in cottonseed meal	144	41	1 : 0.3
" " ammonium sulphate	116	64	1 : 0.6

An examination of the table shows that it is possible to in-

crease the relative numbers of either group of organisms by cultivation in the proper medium. That there are two groups of organisms of this kind is in itself no evidence that organisms exist which oxidize organic matter to nitrates or nitrites, however; for we could assume that the germs which prepare cottonseed meal for nitrification by breaking it down to ammonium salts are diminished in relative number when the organisms are cultivated in a medium containing ammonium salts, and this assumption would, in part, explain the facts here given.

C. It seems probable that there are organisms which nitrify organic matter directly. If they do not exist, it should be possible to increase the rate of nitrification of ammonium salts without increasing the nitrification of cottonseed meal, but it should not be possible to increase the rate of nitrification of cottonseed meal without increasing that of ammonium sulphate, since the organisms which oxidize ammonium salts must increase in the same proportion as those which prepare the cottonseed meal by converting it into ammonium salts. If all the nitrification is effected by oxidation of ammonium salts as an intermediate stage, there should be more of these germs in a soil in which 233 milligrams nitrogen per kilogram are oxidized in the form of cottonseed meal, than where only 190 milligrams are so changed. But in the first case only 162 milligrams nitrogen in the form of ammonium sulphate are nitrified, in the second 200 milligrams. The fact that ammonium salts, in none of the cases mentioned in this article, are nitrified much faster than cottonseed meal, is also in favor of the view that organisms exist which can change organic matter directly to nitrates or nitrites. The only conclusive proof that can be offered is the isolation and study of an organism of this kind, which would not be an easy matter. At present the evidence is certainly in that direction.

PART III.

Determination of the Comparative Nitrifying Power of Soils.

The work recorded in this article serves as a basis for a method of determining the relative nitrifying power of soils,

which it is believed will lead to very important results. The nitrifying properties of soils may be studied with regard to several points:

1. *Number of Germs in the Soil.*—As has been shown in this article, the number of nitrifying organisms in any given soil is subject to wide fluctuations. As the activity of the germs varies as well as their number, it may be said that at present there is no method for comparing the relative number of germs in different soils.

2. *Nature of Germs.*—It is not considered of practical importance to determine the relative numbers of germs in soils which nitrify organic matter, and which nitrify ammonium salts, since it is probable that both groups of organisms are present in every soil, and their numbers may be increased by proper treatment.

3. *Comparative Nitrifying Power of Soils.*—This regards the soil only as a medium for the growth of the nitrifying organisms, and has for its object the comparison of the capacity of different soils to support nitrifying organisms.

In order to compare the nitrifying power of two or more soils, it is necessary that they should be placed under conditions favorable for nitrification, the conditions being exactly alike for each soil, and each soil should contain exactly the same number of nitrifying organisms with the same activity.

Method of Work.

The soils to be tested are sterilized by drying and treatment with chloroform, and are heated again to drive off the chloroform. Inoculation tests are then instituted on the soils as described in the earlier part of this paper. All the soils to be compared should be inoculated at the same time and with the same soil. For a number of soils, a standard soil can be used for comparison. At the end of three weeks, the quantity of nitrates in each soil is a measure of its ability to support the nitrifying organisms under the conditions of the experiment. In many cases it will be found of value to determine the nitrates at the end of the fourth, or even the fifth, week, especially if the soil used for the inoculation has a low inoculation in-

tensity. Where a number of soils are to be studied it would be of advantage to prepare a soil for inoculation with a high inoculation intensity.

Table VI. shows the application of this method to the determination of the relative nitrifying power of three soils.

Table VI.—Relative Nitrifying Power of Soils.

	Milligrams nitrogen per kilogram soil.		
Nutrient.	Poor sandy soil.	Rich sandy soil.	Sandy clay soil.
Cottonseed meal	2	116	..
Ammonium sulphate	3	73	77

The figures are the mean of duplicates. It is seen that the poor sandy soil has little power of nitrification for either ammonium sulphate or cottonseed meal. The nitrifying powers of the soils for cottonseed meal are in the proportion 1 : 58, and for ammonium sulphate, 1 : 24 : 25.

Application of the Method.

As seen above, different soils have very different capacity to support the nitrifying organisms. It is not known clearly why this is so, and how cultivation and treatment of the soil may modify its nitrifying powers. There is a great field for the study of the comparative nitrifying powers of soils in connection with the soil survey going on in the different states. By comparing the nitrifying powers of the different typical soils, it should be possible to divide them into different groups, according to their ability to support the nitrifying bacteria. This classification having been made, it can serve as a basis on which to determine the different factors which influence nitrification in the different typical soils. It will then become possible to control this very important process of nitrification in the field, at least to a large extent.

It is believed that this is a very important field for research, one in which the results will have a bearing of great importance for practical agriculture, and for agricultural chemistry.

Summary.

1. The number of nitrifying organisms in a given soil varies according to the conditions to which the soil is exposed.

2. The activity of the organisms is periodic. There is a period of rapid nitrification, preceded and followed by periods of comparative inactivity.

3. The inoculation intensity of a soil provided with nitrogenous matter, meaning its power to induce nitrification in a sterilized soil, increased with the time during the whole course of the experiments.

4. The nitrifying bacteria probably multiply continuously during such an experiment, and there are periods in which they nitrify very little.

5. It is possible to increase the inoculating power of a soil greatly.

6. The difference in the rate of nitrification of cottonseed meal and of ammonium sulphate in different soils is due to a difference in the organisms in the soils, since the same differences appear in the same sterilized soil inoculated with different nitrifying soils.

7. There are two groups of nitrifying organisms in soils, one of which nitrifies cottonseed meal more readily and the other ammonium sulphate. It is possible to increase the relative numbers of one or the other group by growing them in a soil containing cottonseed meal or ammonium sulphate.

8. Four groups of organisms take part in nitrification: those which convert organic matter to ammonium salts, those which convert ammonium salts to nitrites, those which convert nitrites to nitrates, and those which convert organic matter to nitrites or nitrates.

9. In order to compare the relative value of the medium which different soils offer for the growth of nitrifying organisms, the soils to be compared must be kept under the same conditions, and each soil must contain the same number of nitrifying organisms, of the same degree of activity.

10. A method is described for determining the comparative nitrifying powers of soils.

11. It is believed that the study of the comparative nitrifying powers of soils in connection with different soil types will be of great value as serving as a basis for the study of the different factors which influence nitrification in the different types of soils.

Contributions from the Chemical Laboratory of the Brooklyn Polytechnic Institute.

A SUGGESTED EXPLANATION OF THE REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.

By J. C. Olsen.

The reduction of permanganic acid by manganese peroxide with the evolution of oxygen was discovered by Morse and studied by Hopkins and Walker, working under his direction.[1] He suggested, as an explanation of this, that the manganese peroxide might have the power of polymerizing, and, to satisfy this tendency, might take molecules of manganese peroxide from permanganic acid molecules, thus liberating oxygen.[2] Morse and Byers studied the phenomenon very thoroughly and found many facts which confirm the hypothesis of Morse and Reese.[3] The decomposition does not take place to any marked extent except in acid solution. The action was studied in solutions acidified with nitric and sulphuric acids, respectively, and the surprising fact was noted that, in the presence of nitric acid, the permanganate is decomposed about three times as rapidly as in the presence of an equivalent amount of sulphuric acid. Morse and Byers were unable to suggest any explanation of why this ratio was not identical with that of the relative strengths of the two acids.

One of us and Morse studied this phenomenon for a short time in the laboratory of the Johns Hopkins University. The records of this investigation were lost in a fire that partially destroyed the laboratory. The experiments were repeated by one of us. A carefully standardized solution of potassium permanganate, containing 40 grams of the salt to the liter, was prepared, as well as $\frac{2}{3}$-normal solutions of sulphuric and nitric acids. Glass stoppers were ground into oil sample-bottles of about 125 cc. capacity. It was found that the stoppers could be made gas-tight by wire fasteners. Twenty cc. of the

[1] Morse, Hopkins, and Walker: This Journal, 18, 401.
[2] Morse and Reese: *Ibid.*, 20, 721.
[3] Morse and Byers: *Ibid.*, 23, 313.

permanganate solution were introduced into each bottle with enough standard oxalic acid to reduce one-quarter of the permanganate, and sufficient sulphuric or nitric acid to liberate all of the permanganic acid and leave an excess of 1.5 molecules of monovalent acid for each molecule of undecomposed permanganic acid. The total volume was then made up to 60 cc. Solutions were prepared in which all of the acid was respectively sulphuric and nitric. Other bottles were filled with solutions in which half of the acid was sulphuric and half nitric. Still others were prepared in which 5 and 10 per cent, respectively, of the total acid was sulphuric, the remainder being nitric acid. The bottles were then placed in a thermostat maintained at 35° C. and were fastened to a horizontal shaft which made from 35 to 40 revolutions per minute. The rotation caused the manganese peroxide to drop through the solution twice each revolution. This method of agitation had been found by Morse and Byers to be the most favorable one for the action of the manganese peroxide on the permanganate. After seventy-two hours' agitation, the bottles were opened and the available oxygen remaining in the permanganate and manganese peroxide was determined by means of standard oxalic acid. The results of one of these experiments are given in tabular form below:

Table I.

Volume of $KMnO_4$.	Volume of $KMnO_4$ reduced to MnO_2.	Per cent of total acid. H_2SO_4.	Per cent of total acid. HNO_3.	Volume of $KMnO_4$ decomposed by MnO_2.	Average.	Ratio of $KMnO_4$ decomposed.
cc.	cc.			cc.	cc.	
15	5		100	4.13		
15	5		100	4.33	4.23	3.81
15	5	5	95	2.56		
15	5	5	95	2.69	2.62	2.36
15	5	10	90	2.03		
15	5	10	90	2.15	2.09	1.88
15	5	20	80	1.83		
15	5	20	80	1.84	1.84	1.66
15	5	30	70	1.71		
15	5	30	70	1.69	1.70	1.53
15	5	50	50	1.45	1.48	
15	5	50	50	1.51		1.33
15	5	100		1.10		
15	5	100		1.12	1.11	1.00

Inspection of these results shows that the influence of each acid, when both are present in the same solution, can by no means be calculated from the amount of decomposition produced by each acid when acting alone. When half of the acid present is sulphuric and half nitric, the decomposition is much less than a mean between the amounts of decomposition produced by each acid alone. Even 5 per cent of sulphuric acid reduces the decomposition to 62 per cent of the amount when only nitric acid is present. An explanation of this phenomenon was at first sought by a study of the conditions existing in the permanganate solution.

When both nitric and sulphuric acids were present, the solution contained, besides these acids, their potassium salts, free permanganic acid and potassium permanganate, the ions of these acids, and the potassium ion. It is a well-known fact that the strength of an acid is reduced by the presence of its salts. Calculations based on the dissociation theory and the known concentration of the various salts and acids in the solutions used seemed to show that sulphuric acid would be weakened by the presence of potassium sulphate much more than the nitric acid would be weakened by the presence of potassium nitrate. The calculated decomposition for the solution containing 50 per cent of each acid agreed quite well with that found by experiment. The results of the calculation for the solutions containing 5 and 10 per cent of sulphuric acid did not agree with the experimental results. It was also thought that the potassium might influence the reaction because of its well-known property of combining with the manganese peroxide.

It was therefore thought desirable to carry on the experiments with permanganic acid free from potassium. For this purpose the electrolytic method of preparing permanganic acid was devised.[1] One of us carried out experiments on permanganic acid prepared in this manner and which was free from potassium. The solutions were prepared and shaken in a manner identical with that of the series in which potassium permanganate was used, except that the amount of sulphuric

[1] This JOURNAL, 23, 5, 431.

acid or nitric acid used was less by the amount necessary to neutralize the potassium of the permanganate. The amount of permanganic acid used was equal to that calculated to be equivalent in oxidizing power to 0.800 gram of potassium permanganate. The results are given in the following table:

Table II.

$HMnO_4$. Gram.	$HMnO_4$ reduced to MnO_2. Gram.	Per cent of total acid. H_2SO_4.	HNO_3.	Volume of 4 per cent. $HMnO_4$ decomposed by MnO_2. cc.	Average. cc.	Ratio of $HMnO_4$ decomposed.
0.607	0.152	100		1.34		
0.607	0.152	100		1.34		
0.607	0.152	100		1.43		
0.607	0.152	100		1.40		
0.607	0.152	100		1.28		
0.607	0.152	100		1.32	1.35	1.00
0.607	0.152	50	50	1.41		
0.607	0.152	50	50	1.43	1.42	1.05
0.607	0.152	5	95	1.92		
0.607	0.152	5	95	2.22	2.07	1.53
0.607	0.152		100	3.28		
0.607	0.152		100	3.59		
0.607	0.153		100	3.19		
0.607	0.152		100	3.18		
0.607	0.152		100	3.32		
0.607	0.152		100	3.40	3.33	2.47

These results are the same in general character as those obtained with potassium permanganate. Although the decomposition in the presence of nitric acid alone is relatively not so great as when potassium is present, the peculiar feature remains that 5 per cent of sulphuric acid is able to cause the decomposition to fall from 3.33 cc. to 2.07 cc., while, when the nitric acid is entirely replaced by the sulphuric acid, the amount of decomposition falls only from 2.07 cc. to 1.35 cc. The curves obtained by plotting each set of results are almost identical. As the only condition which had been changed was the removal of the potassium from the solution, it is fair to assume that this element is not the cause of this peculiarity of the decomposition.

Further Study of the Decomposition of Permanganic Acid by Manganese Peroxide.[1]

By J. C. Olsen and F. S. White.

Having failed to find by a study of the solution an explanation of the marked retardation of the rate of decomposition of permanganic acid by manganese peroxide produced by even small quantities of sulphuric acid, the manganese peroxide precipitated under the various conditions involved was investigated. It was first noticed that when manganese peroxide is precipitated by oxalic acid from a solution containing sulphuric acid, it retains, with some persistence, part of the sulphuric acid, while the oxide precipitated from solutions containing nitric acid does not retain a trace of that acid. If both acids are present in the solution, the precipitated manganese peroxide will retain the sulphuric acid only. In each case the precipitate was filtered off on asbestos and washed until the wash-water no longer showed the color of permanganic acid. It was found that the sulphuric acid held by the precipitate could be completely removed by persistent washing with distilled water, about three times as much water being required for this purpose as was necessary to remove the permanganate. A blank test was made in which a solution containing as much sulphuric acid as was used with the permanganate was filtered through asbestos, which was then washed with as much water as had been found necessary to remove the permanganate from the manganese peroxide. The asbestos was then found to be free from sulphuric acid. It would seem, therefore, that, under the conditions studied, sulphuric acid forms a chemical compound with manganese peroxide which is easily dissociated by water, while nitric acid does not form a similar compound.

The frequently observed and striking phenomenon that, when manganese peroxide is dissolved by oxalic acid, the well-known permanganate color is developed for an instant, suggested the idea that manganese peroxide might also enter into chemical combination with permanganic acid. Such a

[1] This work was done in the chemical laboratory of the Polytechnic Institute of Brooklyn.

salt would probably be very unstable, decomposing with evolution of oxygen and the formation of a polymerized manganese peroxide. Morse and Byers[1] have already proved that the oxide remaining after a solution of permanganate had been acted on by manganese peroxide is such a polymerized oxide. If sulphuric acid is present, however, part of the manganese peroxide will combine with it instead of with the permanganic acid. The evolution of oxygen will, therefore, be slow. If only nitric acid is present, all of the manganese peroxide will be free to combine with the permanganic acid, and thus the evolution of oxygen will be rapid. All of the observed phenomena of the reduction of permanganate solutions by means of manganese peroxide can, therefore, be explained by the weak basic properties of manganese peroxide and a tendency to unite with sulphuric acid rather than with the nitric or permanganic acids. The existence of compounds of manganese with chlorine and fluorine, in which the manganese acts as a tetravalent base, has long been recognized.

To test the correctness of this theory, determinations were made of the amount of sulphuric acid held by the manganese peroxide precipitated under the same conditions as when the amount of oxygen evolved was determined. The amount of available oxygen in the manganese peroxide was also determined, since, if the permanganate solution was decomposed by the union of permanganic acid with the manganese peroxide, the latter ought to show, on analysis, a larger per cent of oxygen than the theoretical for MnO_2.

The determinations of sulphuric acid were made as follows: A solution was made containing 0.800 gram of potassium permanganate, and sufficient acid to neutralize all of the potassium and leave 1.5 molecules of free acid for each molecule of permanganic acid. One-fourth of the permanganate was reduced to manganese peroxide by standard oxalic acid and the volume of the solution made up to 60 cc. After standing over night the precipitate was filtered off on asbestos and washed free from permanganate with 50 cc. of water; then further washing with about 150 cc. freed the precipitate from

[1] This JOURNAL, 23, 313.

sulphuric acid, which was precipitated by barium chloride and weighed on a Gooch crucible. As the results were not very concordant, another method of determining the sulphuric acid was adopted. The washings were transferred to a weighed platinum dish, neutralized with freshly distilled ammonia, evaporated to dryness, and brought to constant weight by drying at 110° C. The ammonium sulphate was then volatilized by gently heating the platinum dish, which was again weighed. The residue in the dish was then washed with water and the dish again weighed. In this manner the amount of free sulphuric acid could be calculated from the weight of ammonium sulphate. The amount of sulphuric acid combined as potassium sulphate was found from the loss in weight on washing the residue with water, while a slight amount of manganese peroxide generally remained which was probably present in the solution as manganous sulphate. The results of these experiments are given in the following tables:

Table III.

Per cent of total acid. H_2SO_4.	HNO_3.	Weight of $BaSO_4$ found. Gram.	Equivalent of $BaSO_4$ in H_2SO_4. Gram.	cc. of $\frac{1}{5}$N acid.
100		0.0056	0.0023	0.12
100		0.0073	0.0030	0.16
100		0.0091	0.0038	0.20
100		0.0109	0.0046	0.24
100		0.0137	0.0058	0.31
100		0.0133	0.0056	0.30
50	50	0.0200	0.0084	0.45
50	50	0.0198	0.0083	0.44

Table IV.

Per cent of total acid. H_2SO_4.	HNO_3.	Free H_2SO_4 found. $(NH_4)_2SO_4$. Gram.	Free H_2SO_4 found. H_2SO_4. Gram.	H_2SO_4 as K_2SO_4. K_2SO_4. Gram.	H_2SO_4 as K_2SO_4. H_2SO_4. Gram.
100		0.0055	0.0041	0.0050	0.0028
100		0.0053	0.0039	0.0025	0.0014
50	50	0.0066	0.0049	0.0051	0.0029
50	50	0.0061	0.0048	0.0069	0.0039
5	95	0.0023	0.0017	0.0010	0.0006
5	95	0.0021	0.0015	0.0020	0.0011

It will be noticed that when 50 per cent of the acid present in the solution is sulphuric, the manganese peroxide carries down rather more of this acid than when all of the acid is sulphuric, while when only 5 per cent of the total acid is sulphuric the amount carried down is still nearly half as much as when only sulphuric acid is present. The amount of sulphuric acid held by the precipitate is, therefore, approximately inversely proportional to the amount of oxygen evolved by it. This relation can be seen more clearly by reference to the accompanying curves.

The manganese peroxide which was analyzed for percentage of oxygen was made in the same manner as that which was washed to determine the amount of sulphuric acid held. It was allowed to stand over night in contact with the solution without shaking. It was then filtered off on asbestos and washed free from permanganate. The asbestos, with the precipitate, was transferred to a beaker and treated with an excess of standard oxalic acid solution and sulphuric acid. When the manganese peroxide was dissolved, the excess of oxalic acid was titrated with standard potassium permanganate solution. In this manner the amount of available oxygen was determined. The excess of sulphuric acid was neutralized by shaking the solution with zinc oxide, and the total manganese determined by the Volhard method. By deducting the amount of manganese contained in the standard potassium permanganate which had been added, the amount of manganese contained in the manganese peroxide was obtained. The results obtained by this method were not very concordant. Analysis of manganese peroxide made by the Volhard method gave results above the theoretical for MnO_2.

	Calculated for MnO_2.	Found. I.	II.
O	36.78	37.39	37.36

Another method of analysis was therefore adopted. The available oxygen was obtained by dissolving the manganese peroxide in dilute hydrochloric acid and potassium iodide, the asbestos with the precipitate being transferred to a glass-stoppered bottle, adding an excess of 10 per cent potassium iodide and dilute hydrochloric acid, and allowing the whole to

stand in the cold until the precipitate was completely dissolved. The iodine liberated was then determined by means of standard thiosulphate solution. The solution was then transferred to a platinum dish, an excess of sodium phosphate added, brought to a boil, and cautiously neutralized with recently distilled ammonia. By stirring and slowly adding ammonia, the manganese was precipitated as the crystalline ammonium manganese phosphate. It was ignited and weighed as manganese pyrophosphate. This method gave more concordant results, manganese peroxide made by the Volhard method giving 36.81 per cent of oxygen instead of the theoretical 36.78 per cent. The results of these analyses are given in the two following tables, the first giving the results of the analysis by oxalic acid and the Volhard method, the second giving the results obtained by the iodine and pyrophosphate method:

Table V.—Analysis of Manganese Peroxide by Oxalic Acid and the Volhard Method.

Per cent of total acid.		
H_2SO_4.	HNO_3.	Per cent of oxygen.
	100	37.83
	100	37.88
50	50	37.16
50	50	37.05
50	50	37.00
100		36.66
100		36.47
100		36.79
100		36.87
100		36.98

Table VI.—Analysis of Manganese Peroxide by the Iodometric Method and Precipitation of Manganese as Phosphate.

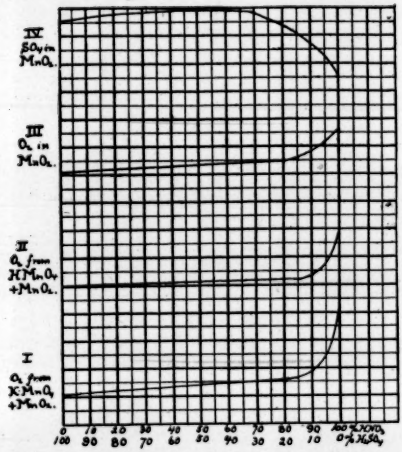
Per cent of total acid.		
H_2SO_4.	HNO_3.	Per cent of oxygen.
	100	38.60
	100	38.91
5	95	38.36
5	95	37.46
50	50	37.80
50	50	36.56
100		36.80
100		37.44

Inspection of this table shows that the highest amount of oxygen found (38.91 per cent) was obtained in the analysis of a precipitate made in the presence of nitric acid, while the lowest (36.47 per cent) was obtained in the analysis of a precipitate made in the presence of sulphuric acid, while when both acids were present the values ranged between these extremes. Considerable variations will be noticed in analyses of precipitates made in apparently the same manner. It must be remembered, however, that the oxygen is held very closely, and is, no doubt, being given off during the manipulation of the precipitate. This instability is well shown by the analysis of the manganese peroxide which has been shaken with the permanganate solution. Under these conditions the oxygen is evolved quite regularly and the precipitate contains approximately the theoretical amount of oxygen for manganese peroxide. These results are given in the following table:

Table VII.—Analysis of Manganese Peroxide which Had Been Shaken with Acid Permanganate Solution.

Per cent of total acid.		
H_2SO_4.	HNO_3.	Per cent of oxygen.
	100	36.79
	100	36.76
5	95	37.22
5	95	36.95
5	95	37.36
5	95	37.00
10	90	36.00
10	90	36.80
50	50	37.11
50	50	37.16
100		37.09
100		36.90

For ease of comparison, the experimental results given in this paper have been plotted as curves. The abscissas of all the curves represent percentages of nitric acid and sulphuric acid in the solution from which the manganese peroxide was precipitated. Curve (1) represents the amount of oxygen evolved from solutions of potassium permanganate. Curve (2) represents the amount of oxygen evolved from solutions of permanganic acid, the conditions being identical with those



of curve (1). The similarity of these curves proves that the peculiarities of the decomposition of the permanganate in the presence of nitric and sulphuric acids is not due to the presence of the potassium. The experimental data of curve (1) are given in Table I., while those of curve (2) are given in Table II. Curve (3) gives the amount of oxygen contained in the manganese peroxide above the theoretical value for manganese peroxide. The experimental data are given in Tables V. and VI. The amount of oxygen held by the precipitate under some conditions seems to be proportional to the amount of oxygen given off from the solution when the conditions favor its evolution. Curve (4) represents the amount of sulphuric acid held by the manganese peroxide. Tables III. and IV. give the experimental data. The amount of sulphuric acid held by the manganese peroxide seems to be inversely proportional to the amount of oxygen held. It seems reasonable to suppose that in this reaction the manganese peroxide acts as a base and combines either with sul-

phuric or permanganic acid. The permanganic permanganate being unstable readily decomposes with evolution of oxygen and the formation of a polymerized manganese peroxide, which is a very much less active compound than the original manganese peroxide. We expect to continue this investigation and hope to get more direct evidence for the existence of a compound of manganese peroxide and permanganic acid.

Contributions from the Chemical Laboratory of Harvard College.

ON THE OXIMES OF NITROMALONIC ALDEHYDE.[1]

By Henry B. Hill and William J. Hale.

In studying the action of hydroxylamine upon nitromalonic aldehyde, Hill and Torrey[2] found that the salts of the nitromalonic dialdoxime could readily be isolated, but, as was to be expected, that the β-nitroisoxazol was the only product which could be obtained under conditions favorable to the formation of the corresponding monoxime. They also found that a complicated reaction ensued when the dialdoxime was liberated by the addition of acid to the aqueous solution of its salts, but they were unable at the time to make a more careful study of the products which were thus formed. We have now made a further investigation of the oximes of nitromalonic aldehyde, and although this study is not yet completed, we think it best to publish the results which we have obtained as we are unable to continue the work together.

We have not succeeded in isolating the nitromalonic dialdoxime, but have found that it is completely decomposed at ordinary temperatures in dilute aqueous solution in the course of a few hours. The most important product of this spontaneous decomposition is fulminuric acid, and its formation shows that the dialdoxime must have retained both of its oxime groups under these conditions. At the same time it affords an interesting confirmation of the formula for fulminuric acid,

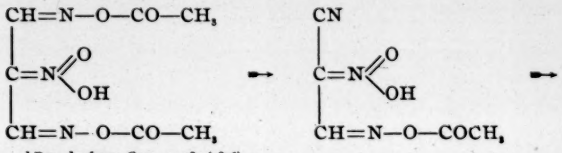
[1] A part of the work described in the following paper formed a portion of a thesis presented to the Faculty of Arts and Sciences of Harvard University in May, 1902, by William J. Hale, candidate for the degree of Doctor of Philosophy.

[2] This Journal, **22**, 89 (1899).

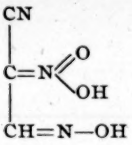
which was suggested by Steiner[1] and afterwards supported by Nef.[2]

As a secondary product of the reaction there is formed in small quantity a crystalline body isomeric with fulminuric acid. We were unable to study it in detail until we found that it could readily be made from the nitromalonic aldoxime nitril or its acetyl derivative, and we shall discuss it more at length in connection with these bodies. Under certain conditions the dialdoxime may also lose a molecule of hydroxylamine, and β-nitroisoxazol is then formed. When a salt of the dioxime is decomposed by the addition of hydrochloric acid, a brilliant, yellow, crystalline body is at first thrown down, but this is so unstable that we have been unable to determine its nature. It may possibly be one form of the dialdoxime which is rapidly isomerized to a more stable configuration.

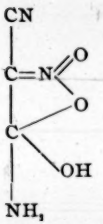
By the action of acetic anhydride upon the sodium salt of the dialdoxime in alkaline solution, the corresponding diacetyl derivative can easily be made. It is acid in its character and forms well-defined salts. This diacetyl derivative or its alkaline salts, by the loss of 2 molecules of acetic acid, is converted into the nitromalonic aldoxime nitril, while the acetyl derivative of the latter appears as an intermediate product.



[1] Ber. d. chem. Ges., 9, 784 (1876).
[2] Ann. Chem. (Liebig), 280, 263 (1894).



The nitromalonic aldoxime nitril is little affected by mineral acids, but it is converted into fulminuric acid by heating its alkaline solution. It forms two sets of salts, but the secondary salts are converted into the primary by the action of carbonic dioxide. If a solution of the secondary salt is acidified with 2 molecules of hydrochloric acid, a crystalline body gradually separates, which has the same composition as the aldoxime nitril, but which is identical in properties with the crystalline substance which is formed in small quantity by the spontaneous decomposition of the nitromalonic dialdoxime. With due care it may be recrystallized from hot water, but if the solution is not quickly cooled it is completely converted into fulminuric acid. By the action of a cold aqueous solution of potassic carbonate, or even of potassic acetate, potassic fulminurate is formed. When heated to 110° it gradually loses in weight, but decomposition soon sets in. We have as yet obtained no more definite evidence as to the structure of the body. Since it appears as an intermediate product between the aldoxime nitril and fulminuric acid, it evidently contains a cyanogen group, but its neutral character apparently excludes the possible presence either of an unaltered oxime or of an isonitro group. Its ready conversion into fulminuric acid is sufficient to show that the isonitro group has remained essentially unaltered, while the oxime group has already nearly completed its passage through the nitril to the amide. In the absence of further evidence, the formula



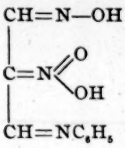
may be suggested as satisfying the conditions already named.

Since the nitromalonic aldoxime nitril is stable in acid solutions, we must conclude that it is isomerized in alkaline solution, as suggested in similar cases by Hantzsch,[1] and later by Abegg,[2] and that the oxime group passes from its *anti-* to its *syn*-form. While the salts of the *syn*-form are comparatively stable, the synoxime itself, when liberated, immediately enters into the reactions necessary to transform it into the amide, but at ordinary temperatures the change is arrested by the formation of the anhydride, and completed only by heat or the possibility of the formation of a salt of fulminuric acid.

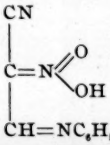
Toward the end of our work we discovered that nitromalonic diacetyldialdoxime under certain conditions lost 2 molecules of acetic anhydride, with the formation of an acid wholly unlike the bodies previously obtained. While we were able to show by analyses of the stable, yellow silver salt that it was isomeric with fulminuric acid, we were unable to study it in detail, and a description of this product must therefore be postponed until the reaction can be more fully investigated.

Hill and Torrey[3] had already observed that aniline hydrochloride reacted upon the sodium salt of nitromalonic dialdoxime with the formation of the corresponding aldoxime anil melting at 162°,

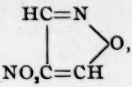
[1] Ber. d. chem. Ges., **28**, 2164 (1892).
[2] *Ibid.*, **32**, 291 (1899).
[3] *Loc. cit.*, p. 108.



and that the same body could also be formed by the action of hydroxylamine upon the nitromalonic aldehyde anil described by them. If this aldoxime anil is heated for a long time with Beckmann's mixture, it loses a molecule of water and is converted into the corresponding nitril which melts at 208° (uncorr.):

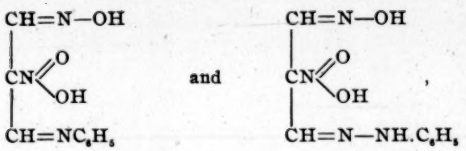


This nitril anil could also be made by the action of aniline hydrochloride upon an alkaline solution of the nitromalonic aldoxime nitril mentioned above, but it especially interested us in that we had already found that it was the chief product formed by the action of aniline upon an alcoholic solution of *β*-nitroisoxazol, a mode of formation which gave little clue to its structure. Since phenylhydrazine, under the same conditions, yields the 1-phenyl-4-nitropyrazol described by Hill and Torrey,[1] with the simultaneous formation of hydroxylamine, it may be assumed that in each case the isoxazol ring,



is opened by addition and the corresponding oximes,

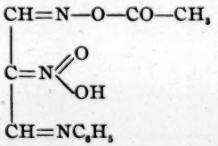
[1] *Loc. cit.*, p. 104.



and

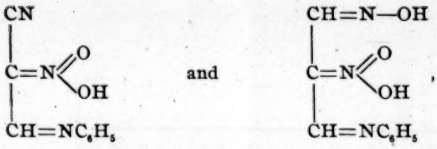
are at first formed. In the case of the aniline derivative the oxime then passes into the nitril by the loss of water, while the stable pyrazol ring is formed by preference from the hydrazone with the elimination of hydroxylamine.

When aniline hydrochloride reacts upon the sodium salt of the nitromalonic diacetyldialdoxime the acetyl derivative of the aldoxime anil,

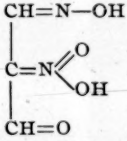


is formed with the simultaneous formation of hydroxylamine, and the same body may easily be made directly from the aldoxime anil by the action of acetic anhydride.

It had already been noticed that a cold aqueous solution of the β-nitroisoxazol soon turned yellow and acquired an acid reaction. We found that 1 molecule of sodic hydrate was apparently required to neutralize the acid which was ultimately formed, but at the same time the behavior of the solution toward aniline showed that no essential decomposition had taken place. On the addition of aniline acetate to the acid solution an abundant precipitate of the nitromalonic nitril anil was soon thrown down, while if sodic hydrate was added to alkaline reaction before the addition of the aniline salt, nitromalonic aldoxime anil was formed. The appearance of these two aniline derivatives,



can be most readily explained by the assumption that the β-nitroisoxazol takes up a molecule of water in dilute aqueous solution and forms the monoxime of the nitromalonic aldehyde,

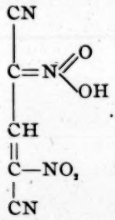


This body is necessarily acid in its character and should pass readily into the anil by the action of aniline. That the unaltered oxime group appears in the product when an aniline salt is added in excess to an alkaline solution, while the corresponding nitril is formed from an acid solution, is, then, due to the stability in alkaline or acid solution of different configurations of the oxime. It must be noted, however, that the direct formation of the synaldoxime from the β-nitroisoxazol and its conversion into the antialdoxime in alkaline solution are not in accordance with the ordinarily accepted theories, and in apparent contradiction to the facts established in the study of the nitromalonic aldoxime nitril.

If the aqueous solution of the β-nitroisoxazol is heated for a short time it becomes bright yellow and strongly acid, as it does on standing for a long time at ordinary temperatures, but aniline now fails to show the presence of either form of the monoxime of the nitromalonic aldehyde. Argentic nitrate, however, throws down a bright-yellow, crystalline, silver salt which has the formula $AgC_5HN_4O_4$, and the mother-liquor contains formic acid in abundance. The simple reaction,

$$2C_3H_3N_3O_3 = C_5H_3N_4O_4 + CH_2O_2,$$

indicates that 2 molecules of the nitromalonic aldehyde monoxime which is first formed are condensed through one aldehyde group, while the second is eliminated as formic acid, the two oxime groups that pass into cyanogen giving the body



Although this formula explains satisfactorily the formation and the properties of the body, we have been able to find no additional evidence in confirmation of it.

Salts of Nitromalonic Dialdoxime.—When the sodium salt of nitromalonic aldehyde is dissolved in a concentrated solution of hydroxylamine hydrochloride, to which a slight excess of sodic carbonate has been added, a pale-yellow, sparingly soluble sodium salt of the corresponding dialdoxime soon separates which, as was shown by Hill and Torrey,[1] contains but a single atom of sodium. Since this salt dissolves readily in alkaline solutions, it seemed to us of interest to determine whether secondary or tertiary salts could not be isolated. The primary sodium salt was therefore suspended in cold water and carried into solution by the addition of 1 and 2 molecules of sodic hydrate. On the addition of alcohol to these solutions, yellow, crystalline salts were obtained which were dried *in vacuo* over sulphuric acid. Analyses of these products showed that they were both essentially the disodium salt, although that prepared with 1 molecule of sodic hydrate contained decidedly too small a percentage of sodium.

I. 0.2156 gram salt gave 0.1552 gram Na_2SO_4.

II. 0.1372 gram salt gave 0.1006 gram Na_2SO_4.

	Calculated for $Na_2C_3H_2N_2O_4$.	Found. I.	Found. II.
Na	24.11	23.34	23.78

[1] *Loc. cit.*, p. 108.

On the addition of argentic nitrate to a solution of the disodium salt, a voluminous, yellow precipitate was thrown down, but it blackened rapidly on exposure to diffused daylight, while the primary salt had previously been shown to be extremely stable.

0.1840 gram salt gave 0.1471 gram AgCl.

	Calculated for $Ag_2C_3H_2N_2O_4$.	Found.
Ag	59.78	60.17

Nitromalonic Dialdoxime.—We have been unable to isolate the nitromalonic dialdoxime from its salts, although we have been able to prove that it exists for a short time in dilute aqueous solution. When a slight excess of hydrochloric acid is added to the sodium salt suspended in water, a bright-yellow, crystalline body is formed, which gradually disappears; if little water is used, the yellow crystals are replaced by colorless plates of the β-nitroisoxazol, or if more water is added, the yellow body dissolves and ether then extracts the nitroisoxazol melting at 46° to 47°. When the sodium salt is suspended in ether and 1 molecule of hydrochloric acid is added with constant shaking, an ethereal solution is obtained which throws down a yellow, crystalline precipitate on the addition of ligroin, but in this case also the color soon fades and the nitroisoxazol alone can be isolated. No more satisfactory results could be obtained by the addition of the requisite amount of an ethereal solution of hydrochloric acid to the salt suspended in ether. In each case the dioxime had evidently been decomposed into β-nitroisoxazol and hydroxylamine according to the equation

$$C_3H_4N_4O_4 = C_3H_2N_2O_4 + NH_4OH.$$

When exactly 1 molecule of hydrochloric acid was added in dilute solution, the yellow body was thrown down and disappeared, and β-nitroisoxazol could be extracted with ether, but the deep-red, aqueous solution gave reactions which showed that it contained unaltered nitromalonic dialdoxime in abundance. On the addition of aniline acetate a yellow, crystalline precipitate was soon formed which melted at 161°

to 162° after recrystallization from alcohol, and was in other respects identical with the nitromalonic aldoxime anil which Hill and Torrey had made by the action of aniline hydrochloride upon the sodium salt of the nitromalonic dialdoxime. When the solution was made alkaline with sodic hydrate, and was then shaken with acetic anhydride, the sodium salt of the nitromalonic diacetyldialdoxime, which we shall describe later, was immediately formed. The solution also gave with ferrous sulphate an intense red color, which became violet on the addition of sodic hydrate, color reactions which had already been mentioned by Hill and Torrey in their description of the nitromalonic dialdoxime. The deep-red solution of the dialdoxime gradually turned yellow on standing, and no longer gave any indication of the presence of the dioxime. In the course of twenty-four hours, slender, colorless needles were deposited, which were sparingly soluble in cold water and neutral in their reaction toward litmus. This body was formed in such small quantity that we were unable to study it in detail. We found that it was identical in composition with fulminuric acid, and that it could be converted into this acid by boiling it with water for a few minutes. Fortunately, we afterwards found that it could easily be made from the nitromalonic acetylaldoxime nitril, which we shall describe later, and a further account of it will be given in that connection. The strongly acid solution was neutralized with potassic carbonate and evaporated to a small volume. On cooling, fine, silky needles separated in abundance, which could easily be purified by recrystallization from hot water. As the silver salt proved to be sparingly soluble and could be crystallized from boiling water without decomposition, it was prepared and purified for analysis.

I. 0.2975 gram substance gave 0.2359 gram AgBr.

II. 0.2343 gram substance gave 0.1346 gram CO_2 and 0.0248 gram H_2O.

III. 0.2217 gram substance gave 34.2 cc. moist N at 18°.5 and 766 mm. pressure.

	Calculated for $AgC_3H_3N_3O_3$.	Found. I.	II.	III.
Ag	45.71	45.56	....	....
C	15.25	....	15.67	....
H	0.85	....	1.18	....
N	17.84	....	....	17.89

The composition of the salt and its physical properties warranted the conclusion that it was argentic fulminurate, and this conclusion was confirmed by the preparation of the characteristic cuprammonium salt, and by comparison with material obtained from mercuric fulminate. The acid itself was readily soluble in water or alcohol, very sparingly soluble in ether, and insoluble in chloroform, benzol, or ligroin. In a capillary tube it melted with decomposition at temperatures which varied from 136° to 149°, according to the rate of heating. The yield of potassic fulminurate was somewhat more than 30 per cent of the amount demanded by the equation

$$C_3H_5N_3O_4 = C_3H_3N_3O_3 + H_2O.$$

No other definite products of the reaction were isolated, but the behavior of the solution toward silver and copper salts showed that hydroxylamine had also been formed.

In order to assure ourselves that the conversion of the dialdoxime into fulminuric acid was not brought about by a slight accidental excess of hydrochloric acid, the well-washed silver salt was treated with pure hydrochloric acid, care being taken that a part of the silver salt remained unaltered. The filtered solution was found to be free from silver and hydrochloric acid, and gave an intense color reaction with ferrous sulphate. After standing for two hours at ordinary temperature the solution still turned slightly red, but at the end of three hours it gave absolutely no color with a ferrous salt. After the lapse of twenty-four hours a very slight crystalline precipitate had separated. The clear solution gave, with argentic nitrate, a yellowish, crystalline precipitate from which argentic fulminurate could be extracted with boiling water. No β-nitroisoxazol could be isolated with ether, but the ether left, on evaporation, a very small amount of a yellow oil which gave, with argentic nitrate, a yellow, microcrystalline precipitate. After thorough

extraction with ether the aqueous solution yielded long, colorless needles of argentic fulminurate on the addition of a crystal of argentic nitrate. On warming the solution from which the argentic fulminurate had been removed, with a drop of ammonic hydrate, metallic silver separated in abundance. In a solution absolutely free from hydrochloric acid the nitromalonic dialdoxime had therefore been partially converted into fulminuric acid, but at the same time a part of it had been decomposed with the formation of hydroxylamine.

Nitromalonic Diacetyldialdoxime.—When the sodium salt of nitromalonic dialdoxime is shaken in alkaline solution with acetic anhydride, the corresponding diacetyl derivative is immediately formed, and its sodium salt separates in the form of pale-yellow, finely felted needles. The salt may be purified by recrystallization from alcohol, and then forms small, obliquely truncated prisms.

I. 0.2486 gram salt gave 0.0702 gram Na_2SO_4.

II. 0.1798 gram salt gave 27.0 cc. moist N at 22°.2 and 762 mm. pressure.

	Calculated for $C_7H_8N_2O_6Na$.	Found. I.	II.
Na	9.10	9.15	....
N	16.63	....	16.95

When quickly heated, the salt melts at 136° to 138° with decomposition and slight explosion, but when slowly heated it is decomposed at a lower temperature. It dissolves readily in warm water, but decomposition soon ensues with the formation of the acetylaldoxime nitril, which is described below. Various salts may be made from it by double decomposition, but none of them have been further examined. When warmed with 2 molecules of sodic or potassic hydrate a deep-red solution is obtained, which contains the alkaline salt of an acid isomeric with fulminuric acid. This reaction is now under investigation.

The ready decomposition in aqueous solution made it advisable to use absolute ether in the preparation of the free diacetyldialdoxime. The salt was therefore suspended in dry ether and an ethereal solution of hydrochloric acid added with

constant shaking. The ethereal solution was then evaporated and the clustered needles thus obtained were recrystallized from ether with the addition of a little ligroin. As the body was found to lose acetic acid on standing for some time over sulphuric acid, it was analyzed after it had been dried for a few hours in a desiccator.

I. 0.1404 gram substance gave 0.1862 gram CO_2 and 0.0530 gram H_2O.

II. 0.1720 gram substance gave 28.6 cc. moist N at 23° and 757 mm. pressure.

	Calculated for $C_7H_9N_3O_8$.	Found. I.	II.
C	36.34	36.18	....
H	3.92	4.22	....
N	18.23	....	18.58

The nitromalonic dialdoxime crystallizes in globular aggregations of fine, colorless needles which melt at 64° to 66°. It dissolves readily in alcohol or chloroform, more sparingly in ether or benzol, but it is nearly insoluble in ligroin or carbonic disulphide.

Nitromalonic Acetylaldoxime Nitril.—When the sodium salt of nitromalonic diacetyldialdoxime is dissolved in water by the aid of gentle heat, decomposition ensues and, on cooling, crystals of the corresponding acetylaldoxime nitril are deposited, while the solution contains acetic acid. The same products result from the spontaneous decomposition of the diacetyldialdoxime already mentioned. We have obtained the best results by suspending the sodium salt in ten times its weight of water and heating at 65° to 70° until complete solution is effected. On cooling, nearly 60 per cent of the theoretical amount of the new product may be obtained.

I. 0.1294 gram substance gave 0.1668 gram CO_2 and 0.0382 gram H_2O.

II. 0.0882 gram substance gave 18.9 cc. moist N at 17° and 764 mm. pressure.

	Calculated for $C_5H_5N_3O_4$.	Found. I.	II.
C	35.05	35.16	....
H	2.94	3.30	....
N	24.61	....	24.89

The nitromalonic acetylaldoxime nitril crystallizes in long, pointed prisms which melt at 87° to 88° (corr.). It is readily soluble in alcohol, ether, benzol, or chloroform; sparingly soluble in carbonic disulphide, and still more sparingly soluble in ligroin. It may be most easily brought to its proper melting-point by recrystallization from ether. It dissolves freely in hot water, but at 100° acetic acid and nitromalonic aldoxime nitril are gradually formed. Even at 70° the same reaction slowly takes place, and in the method of preparation which we describe, the aldoxime nitril is found in the mother-liquors in considerable quantities. In alkaline solutions, salts of the aldoxime nitril are at once formed.

Nitromalonic Aldoxime Nitril.—The nitromalonic aldoxime nitril may easily be made by heating its acetyl derivative for some time at 100° with a small quantity of water. The reaction is much facilitated by the addition of a small amount of hydrochloric acid, and is then completed in the course of a few minutes. A part of the product separates as the solution cools and more may be obtained by concentration of the mother-liquor. The body was purified for analysis by recrystallization from hot water.

I. 0.1944 gram substance gave 0.1976 gram CO_2 and 0.0432 gram H_2O.

II. 0.0790 gram substance gave 22.6 cc. moist N at 20° and 761 mm. pressure.

	Calculated for $C_3H_3N_3O_3$.	Found. I.	Found. II.
C	27.88	27.73	....
H	2.34	2.49	....
N	32.62	....	32.62

The nitromalonic aldoxime nitril crystallizes in long, colorless, dendritic needles, or from concentrated solutions in irregularly aggregated prisms, which melt at 143° to 144° (corr.). It is readily soluble in alcohol, ether, or hot water, sparingly soluble in cold water, chloroform, or benzol, and nearly insoluble in carbonic disulphide, or ligroin. It is but slowly attacked by mineral acids, but after heating for three hours in a sealed tube at 100° with concentrated hydrochloric

acid, it was found to be partially decomposed. The acid solution gave with silver and copper salts qualitative reactions for hydroxylamine. With acetic anhydride it readily forms the acetyl derivative which has just been described, but we have not yet been able to convert this acetyl derivative or the aldoxime itself into the corresponding nitromalonic nitril. The aldoxime dissolves promptly in solutions of the alkaline carbonates, and its salts may also conveniently be prepared by the action of caustic alkalies upon the acetyl derivative. In any case it was evident that two different salts could be made by varying the amount of the alkaline hydrate used. The sodium salts proved to be difficult of purification and we therefore prepared the dibarium salt for analysis, and from this the primary silver salt.

When the nitromalonic aldoxime or its acetyl derivative is dissolved in a cold saturated solution of baric hydrate, the dibarium salt gradually separates in pale-yellow, clustered needles. On heating, the salt turns a deeper yellow with the loss of water. Since the salt was decomposed by carbonic dioxide it was heated in a current of dry, purified air in order to determine the water of crystallization.

I. 0.2816 gram air-dried salt gave 0.2183 gram $BaSO_4$.

II. 0.2218 gram air-dried salt lost, at 155°, 0.0268 gram H_2O.

	Calculated for $C_3HN_2O_3Ba.2H_2O$.	Found. I.	Found. II.
Ba	45.72	45.63	....
H_2O	11.99	....	12.09

This barium salt was suspended in water and decomposed with carbonic dioxide. On the addition of argentic nitrate to the filtered solution a pale-yellow, silver salt was thrown down in short, clustered needles, which proved, on analysis, to contain but 1 atom of silver.

0.1446 gram salt gave 0.1154 gram AgBr.

	Calculated for $AgC_3H_2N_2O_3$.	Found.
Ag	45.72	45.84

On the addition of aniline hydrochloride to an alkaline solution of the aldoxime nitril, the nitromalonic anil nitril, which

we shall soon describe, was at once formed. After one recrystallization from glacial acetic acid it melted at 206° to 207° (uncorr.). When the aldoxime nitril is heated with an excess of potassic hydrate, fulminuric acid is soon formed.

If hydrochloric acid is added to a solution of a salt of the aldoxime nitril in precisely the amount required to liberate the oxime, the solution at first remains clear, but on standing it gradually deposits long, slender needles of a body isomeric with the aldoxime. The yield amounts to about 75 per cent of the weight of the oxime taken. The mother-liquor contains fulminuric acid, but no unaltered oxime could be detected. The body proved to be identical with the sparingly soluble product formed in small quantities by the spontaneous decomposition of the dialdoxime in aqueous solution. It is also formed, together with fulminuric acid, by the action of hydroxylamine upon β-nitroisoxazol. As we were unable to recrystallize the body without effecting a more or less complete isomerization, it was washed well with cold water and dried over sulphuric acid. The material obtained from the dialdoxime was barely sufficient for the analyses necessary to establish its composition.

I. 0.2126 gram substance gave 0.2174 gram CO_2 and 0.0526 gram H_2O.

II. 0.1162 gram substance gave 33.5 cc. moist N at 22° and 759 mm. pressure.

	Calculated for $C_3H_3N_3O_3$.	Found. I.	II.
C	27.88	27.90	....
H	2.34	2.77	....
N	32.62	....	32.46

The body is very sparingly soluble in all ordinary organic solvents. It is also very sparingly soluble in cold water, but it dissolves freely on heating. If the hot solution is quickly cooled, a portion of the substance again separates in crystalline form, but if great care is not taken the body is completely converted into fulminuric acid and the solution remains clear on cooling. The body slowly dissolves in solutions of the alkaline carbonates with the formation of the corresponding

salts of fulminuric acid. When triturated with concentrated solutions of potassic carbonate or potassic acetate, it soon gives, in the cold, the finely felted needles of potassic fulminurate. In a capillary tube it melts with decomposition at from 128° to 140°, according to the rate of heating. When heated at 110° it slowly loses in weight, but the loss in weight is evidently attended by decomposition. As yet we have been unable to prepare from this body any derivatives which establish its structural relations to fulminuric acid.

Nitromalonic Acetylaldoxime Anil.—Hill and Torrey[1] have already described the product which is formed when aniline hydrochloride is added to a solution of the sodium salt of the nitromalonic dialdoxime. One oxime group is eliminated in the form of hydroxylamine, and the crystalline nitromalonic aldoxime anil melting at 162° (uncorr.) is at at once thrown down. They have also shown that the same body may be made by the action of hydroxylamine upon the nitromalonic aldehyde anil. If this aldoxime anil is warmed with eight or ten times its weight of acetic anhydride, the acetyl derivative is soon formed. As the solution cools, a part of the product separates in crystalline form, and the rest may be precipitated by dilution with water. This same acetyl derivative may be prepared more conveniently by the action of aniline hydrochloride upon the sodium salt of the nitromalonic diacetyldialdoxime. The product is somewhat viscous at first, but soon becomes crystalline, and the yield is over 80 per cent of the theoretical amount. In this case hydroxylamine is formed and is readily isolated from the mother-liquor. For its identification we added the hydrochloride to an alkaline solution of the nitromalonic aldehyde anil and obtained the aldoxime anil, which melted at 160° to 161° after one recrystallization from alcohol.

0.1802 gram substance gave 26.7 cc. moist N at 18° and 759 mm. pressure.

	Calculated for $C_{11}H_{11}N_3O_4$.	Found.
N	16.90	17.01

[1] *Loc. cit.*, p. 108.

The nitromalonic acetylaldoxime anil is readily soluble in alcohol, chloroform, benzol, or glacial acetic acid, less readily soluble in ether, and is sparingly soluble in carbonic disulphide or ligroin. It is insoluble in water, but is slowly decomposed by boiling water. From glacial acetic acid it crystallizes in yellow, radiating needles, or on slow cooling in well developed, obliquely truncated prisms. After repeated recrystallization from alcohol it melted at 114° to 115°, but crystallization from carbonic disulphide raised the melting-point to 115° to 116° (corr.). When gently warmed with dilute sodic hydrate it is immediately decomposed, and hydrochloric acid then precipitates the aldoxime anil melting at 162°.

Nitromalonic Nitril Anil.—The nitromalonic acetylaldoxime anil remains unchanged even after long heating with an excess of acetic anhydride, but with Beckmann's mixture it gradually passes into the nitril. The reaction is slow, and even after long boiling in a stream of gaseous hydrochloric acid but a small yield of the nitril is obtained. Still we had little difficulty in preparing in this way sufficient material to enable us to establish its identity. The excess of acetic acid was driven off on the water-bath, and the dark yellow crystals which separated on cooling were recrystallized from glacial acetic acid. The body then melted at 205° to 208° and was, in other respects, identical with material prepared by more convenient methods. The substance may be made most readily by the action of aniline upon an alcoholic solution of β-nitroisoxazol. If somewhat more than one molecule of aniline is added at ordinary temperatures, the nitril anil soon begins to separate, and in a short time the reaction is complete. The yellow crystalline precipitate is sparingly soluble in alcohol, and may be purified most conveniently by crystallization from glacial acetic acid or ethyl acetate.

I. 0.1843 gram substance gave 0.3866 gram CO_2 and 0.0767 gram H_2O.

II. 0.1642 gram substance gave 32.9 cc. moist N at 22°.5 and 758 mm. pressure.

	Calculated for $C_9H_7N_3O_4$.	Found. I.	II.
C	57.09	57.23	....
H	3.73	4.66	....
N	22.26	....	22.48

The nitromalonic nitril anil is insoluble in water and sparingly soluble in alcohol, ether, chloroform or benzol. It dissolves freely in hot glacial acetic acid, and, as the solution cools, it separates in compactly clustered, short, yellow prisms which melt at 208° (uncorr.). It dissolves quite readily in boiling ethyl acetate, and repeated recrystallization from this solvent gave the somewhat higher melting-point, 209° to 210° (uncorr.) or 215° to 216° (corr.). It dissolves promptly in cold dilute sodic hydrate and is reprecipitated unchanged on the addition of acids, but hot or concentrated sodic hydrate liberates aniline.

Reactions with Phenylhydrazine.—Phenylhydrazine was found to react upon β-nitroisoxazol in alcoholic solution with the evolution of heat, and as the solution cooled a somewhat dark-colored crystalline product separated. After recrystallization from alcohol, the substance melted at 126° to 127° (uncorr.) and proved to be identical in properties with the 1-phenyl-4-nitropyrazol described by Hill and Torrey[1] as formed from nitromalonic aldehyde by the action of phenylhydrazine. From the mother-liquors a white crystalline hydrochloride was obtained which gave, when heated with benzophenone, the corresponding oxime melting at 138° to 139°. The chief products of the reaction were, therefore, 1-phenyl-4-nitropyrazol and hydroxylamine. When phenylhydrazine hydrochloride is added to an aqueous solution of the sodium salt of the nitromalonic dialdoxime, an orange-red, viscous precipitate is thrown down which soon becomes crystalline; on standing, the orange-red color soon passes into a dull brown. The crystalline product was dried and recrystallized from a mixture of ether and ligroin without the aid of heat. The melting-point, 126° to 127°, and other properties of the body showed that it was 1-phenyl-4-nitropyrazol. The orange-red needles which were formed at first were doubtless

[1] *Loc. cit.*, p. 104.

the unstable aldoxime hydrazone corresponding to the stable aldoxime anil which is formed under similar conditions by the action of aniline hydrochloride.

Action of Water upon β-Nitroisoxazol.—An aqueous solution of β-nitroisoxazol is at first apparently neutral to litmus, but it rapidly acquires an acid reaction and at the same time it turns bright yellow. We thought it of interest to determine, by titration, the amount of acid which was thus ultimately developed, although the rapid alteration of the nitroisoxazol in neutral solution made it impossible to determine by this method the percentage which remained unchanged in the acid solution at any given time. A decinormal solution of the nitroisoxazol was accordingly titrated with N/10 sodic hydrate after standing at ordinary temperatures for one, two, and three days. With phenolphthalein a satisfactory end-point could be obtained, and in each case 1.004 molecules of sodic hydrate were required for 1 molecule of the nitroisoxazol. These figures made it probable that no more essential alteration of the nitroisoxazol had taken place than was involved in its conversion into the nitromalonic aldehyde aldoxime by the addition of a molecule of water, or in its direct isomerization into nitromalonic aldehyde nitril. Either product would require 1 molecule of sodic hydrate for its neutralization. An examination of the acid solution showed that it doubtless contained the aldehyde aldoxime. On extraction with ether β-nitroisoxazol could be recovered, which melted at 46° to 47°, after recrystallization from ether and ligroin. When aniline or aniline acetate was added directly to the acid solution, a crystalline precipitate of the nitromalonic nitril anil soon separated, which could easily be identified by its melting-point, 207° to 208°, and its other properties; but if the solution was first made alkaline with sodic hydrate and an aniline salt then added in excess, nitromalonic aldoxime nitril melting at 161° to 162° was at once formed. As the solution stands, the yield of these two aniline derivatives diminishes from day to day, and the color of the precipitates obtained gradually becomes dark-brown instead of yellow. Finally the solution no longer reacts with aniline, but gives a flocculent

precipitate with argentic nitrate and gives qualitative tests for hydrocyanic and formic acids.

If β-nitroisoxazol is heated for a short time with water at 100°, a deep yellow, strongly acid solution is obtained, which does not react with aniline. If the solution is not heated too long, it gives, on the addition of argentic nitrate, beautiful long, yellow needles of a silver salt, which is sparingly soluble even in boiling water, but which may readily be recrystallized from very dilute nitric acid. The mother-liquors, on standing, gradually deposit a pale yellow, amorphous salt, which is apparently a mixture, but when boiled with dilute nitric acid it yields an additional quantity of the yellow crystalline salt (Analyses II and III). For analysis the salt was dried at 100° to 105°.

I. 0.1730 gram salt gave 0.1122 gram AgBr.

II. 0.1261 gram salt gave 0.0817 gram AgBr.

III. 0.1518 gram salt gave 0.0984 gram AgBr.

IV. 0.1662 gram salt gave 0.1256 gram CO_2 and 0.0106 gram H_2O.

V. 0.1722 gram salt gave 29.7 cc. moist N at 22°.2 and 759 mm. pressure.

VI. 0.1561 gram salt gave 27.2 cc. moist N at 23°.8 and 767 mm. pressure.

	Calculated for $AgC_5HN_4O_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Ag	37.33	37.27	37.22	37.25	....	....	....
C	20.75	....	....	....	20.62	....	....
H	0.35	....	....	....	0.71	....	....
N	19.43	....	....	....	....	19.40	19.65

The silver salt, when decomposed by dilute hydrochloric acid, gives a yellow acid solution which, on evaporation, or extraction with ether, yields a yellow, viscous syrup. From this viscous residue the crystalline silver salt may again be made without difficulty, but we have as yet been unable to prepare from it, or from the silver salt, other crystalline derivatives.

To the mother-liquor obtained in the preparation of the silver salt, sodic chloride was added until the whole of the silver

which it contained was precipitated, and the filtered solution was then distilled. The acid distillate contained formic acid in abundance, as was shown by qualitative test, and also by the analysis of the lead salt which was made from it by neutralization with plumbic carbonate.

0.2546 gram salt gave 0.2592 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.53

Contributions from the Chemical Laboratory of Case School of Applied Science.

A METHOD FOR DETERMINING THE INDEX OF REFRACTION OF SOLID HYDROCARBONS WITH THE PULFRICH REFRACTOMETER.

INDEX OF REFRACTION OF THE SOLID HYDROCARBONS IN PETROLEUM.[1]

By Charles F. Mabery and Lee Shepherd.

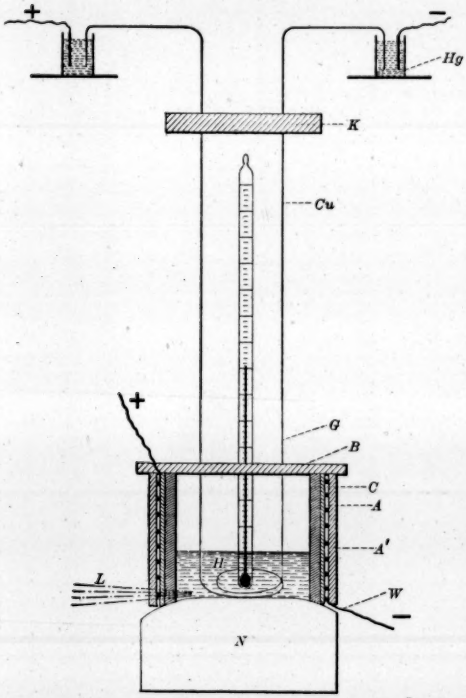
One of the most important physical constants of liquids is the index of refraction from which the molecular refraction may be calculated. Of the two forms of apparatus in use for these determinations, the Abbé and Pulfrich refractometers, the latter is in all respects the most convenient. But neither refractometer as constructed permits of the determination of the index of solid bodies, which requires a rise in temperature sufficient to liquefy the solid. So far as we are aware, no method has been proposed for determining the index of solids. The only method suggested for ascertaining the index of liquids at increased temperatures is that of Brühl,[2] which depends on raising the temperature to the desired point by means of a copper bar of peculiar shape, extending to a sufficient distance from the prism to be heated by a lamp. Sufficient heat is applied to the bar to reach the desired temperature over the prism by conduction. A stirrer is also attached to insure equal heating of the liquid.

[1] The solid hydrocarbons used in the preparation of this paper were prepared in the work carried on with aid granted by the Academy of Arts and Sciences from the C. M. Warren Fund for Chemical Research.

[2] Ber. d. chem. Ges., 24, 286 (1891).

But this method is not satisfactory, especially for solids, since they require temperatures for melting that are difficult to maintain constant by external application without breaking the joint between the prism and the glass cup which holds the liquid. It occurred to us that a more convenient source of heat for melting solids might be supplied by means of an electric current passing through a wire of suitable size to afford the necessary resistance. After numerous experiments, that need not be described in detail, it was found that the heat from a coil of wire surrounding the glass cup containing the substance, even with a sheet of asbestos interposed, caused such unequal expansion of cup and prism that the lute cracked, causing leaks at the joint. On trying to maintain the desired temperature by a coil of wire placed within the glass cup it was found difficult to regulate the temperature at just the point desired. Finally it was found that a coil of wire surrounding the glass cup could be relied on to raise the temperature nearly to the point desired, and by means of an inner coil the temperature just required for melting could be obtained. German silver wire was found to be more suitable for the coils on account of its rigidity, and the size selected was No. 25 English standard gauge. The arrangement of outside and inside coils, prism, glass cup, and attachment for stirring the melted solid are shown in the figure.

The outer coil of wire *W*, is drawn over a thin sheet of asbestos *A*, which surrounds the glass cup, and another thicker sheet is placed outside to prevent radiation. German silver wire of the same size is used for the inner coil and connected above the glass cup to longer copper conductors, which are bent twice so as to dip into mercury cups. This coil is kept in place by means of a cork support *K*, and the asbestos cover *B*, which also serves to retain the heat. The inner coil also serves as a stirrer by moving it up and down, which is possible on account of the deep mercury cups. In this manner the solid, after melting, is very evenly heated. The solid is placed in the glass cup on the face of the prism *N*, melted by the heated wire, and the temperature kept constant by the inner coil, as indicated by the thermometer.



The rays of light *L* enter the prism through a slit in the asbestos, 0.5 cm. square. A current of 3 to 5 amperes was sufficient to maintain the temperatures desired in these determinations. With this combination of internal and external heating a temperature of 100° may readily be kept constant without fear of breaking the joint between the prism and glass cup.

The accuracy of this method of heating was determined with water with the following results:

	20°.	30°.	40°.	50°.	60°.	70°.
Angle	67°38′	67°51′	68°10′	68°10′	68°48′	70°9′
Index of refraction	1.3313	1.3304	1.3291	1.3276	1.3241	1.3208
Molecular refraction	3.692	3.692	3.692	3.692	3.691	3.692

Theoretical molecular refraction of water, 3.692.

This method was applied to the determination of the index of refraction of hydrocarbons separated from Pennsylvania petroleum direct, as described by one of us (Mabery) in a former paper,[1] and also to the same hydrocarbons separated from commercial paraffin. The bodies from crude petroleum had been distilled many times under a tension of 50 mm. and separated from the liquid hydrocarbons by cooling to a low temperature, pressing out the liquid hydrocarbon, and crystallization of the solids from ether and alcohol.

Attempts were first made to ascertain the index directly by melting the solid on the face of the prism, but on account of lack of uniformity in melting, a thin film of the solid persisted on the face of the prism and obstructed the passage of light. The method of mixture was, therefore, resorted to with perfect success. Readings of angles were taken at temperatures above the melting-points of the solids and the density of the solids was taken at the same temperatures. The solvent selected was a petroleum distillate with high boiling-point, 202° to 203°, 50 mm. that had been fractioned many times. It was essentially pure $C_{18}H_{38}$. On account of its high boiling-point there was no danger of loss by vaporization during the observations. The index and specific gravity of the solvent were determined at 60°, 70°, and 80°. The specific gravity was in all cases referred to water at 4°.

The following values were given by the solvent oil:

	Specific gravity.	Angle of refraction.	Index of refraction.
60°	0.7785	49° 6′	1.4341
70°	0.7722	49° 35′	1.4311
80°	0.7612	50° 16′	1.4277

The results of the observations were calculated by the formula for mixtures:

[1] Proc. Am. Acad., 32, 365 (1902); This JOURNAL, 28, 165 (1902).

$$\frac{n-1}{d}\ 100 = \frac{n_1-1}{d_1} + \frac{n_2-1}{d_2}\ (100-p).$$

n = index of mixture
n_1 = " " solvent
n_2 = " " solid
d = density of mixture
d_1 = " " solvent
d_2 = " " solid
} all taken at t°
p = per cent of solvent
$(100-p)$ = " " solid

The mixtures were made of such proportions that each contained approximately 20 per cent of the solid, and 2 grams were necessary for each determination, one-half the full capacity of the cup, which was necessary to maintain a uniform temperature. The index and specific gravity of each solid were taken at two temperatures, 60° and 70°, or 70° and 80°.

The following results were obtained with the hydrocarbons from Pennsylvania petroleum:

Distillate, 50 mm. 260° to 262°. $C_{23}H_{48}$.
Per cent of solvent, 77.86.
Per cent of solid, 22.14.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n_2.
60°	0.7780	0.7769	49° 9′ 3″	1.4337
70°	0.7711	0.7709	49° 43′	1.4304

Calculated for solid:

	n_2.	Molecular refraction.	Theoretical.
60°	1.4432	110.61	
70°	1.4260	107.68	107.68

Distillate, 50 mm. 272° to 274°. $C_{24}H_{50}$.
Per cent of solvent, 82.53.
Per cent of solid, 17.47.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n_2.
60°	0.7785	0.7771	49° 5′ 3″	1.4341
70°	0.7734	0.7719	49° 40′	1.4307

Calculated for solid:

	n_2.	Molecular refraction.	Theoretical.
60°	1.4432	113.08	
70°	1.4251	112.00	112.57

Distillate, 50 mm. 282° to 284°. $C_{28}H_{58}$.
Per cent of solvent, 84.03.
Per cent of solid, 15.97.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7724	0.7765	49° 50′	1.4297
80°	0.7618	0.7632	50° 23′ 8″	1.4263

Calculated for solid :

	n_D.	Molecular refraction.	Theoretical.
70°	1.4241	115.0	
80°	1.4212	117.0	117.2

Distillate, 50 mm. 292° to 294°. $C_{28}H_{58}$.
Per cent of solvent, 83.13.
Per cent of solid, 16.87.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7726	0.7780	49° 38′	1.4309
80°	0.7618	0.7685	50° 13′ 7″	1.4373

Calculated for solid :

	n_D.	Molecular refraction.	Theoretical.
70°	1.4320	122.0	
80°	1.4305	123.2	121.8

Distillate, 50 mm. 300° to 301°. $C_{21}H_{44}$.
Per cent of solvent, 77.64.
Per cent of solid, 20.36.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7719	0.7757	49° 55′	1.4292
80°	0.7623	0.7655	50° 29′ 4″	1.4257

Calculated for solid :

	n_D.	Molecular refraction.	Theoretical.
70°	1.4206	124.2	
80°	1.4194	125.45	126.4

Distillate, 50 mm. 312° to 314°. $C_{29}H_{60}$.
Per cent of solvent, 86.79.
Per cent of solid, 13.21.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7738	0.7770	49° 40′ 6″	1.4297
80°	0.7618	0.7669	50° 14′ 6″	1.4272

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
70°	1.4184	126.6	
80°	1.4170	128.8	131

Having at hand a series of solid hydrocarbons separated from commercial paraffin, that correspond in composition to the solid hydrocarbons from crude Pennsylvania petroleum, determinations of the indices of refraction of these bodies were made for the purpose of comparison. The formulas of the paraffin hydrocarbons are given as they have been determined, although the results have not been published.

Distillate, 50 mm. 260° to 262°. $C_{22}H_{46}$.

Per cent of solvent, 79.84.

Per cent of solid, 20.16.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
60°	0.7780	0.7706	49° 16′ 5″	1.4330
70°	0.7668	0.7641	49° 44′	1.4303

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
60°	1.4256	106.7	
70°	1.4374	111.0	108.0

Distillate, 50 mm. 282° to 286°. $C_{23}H_{48}$.

Per cent of solvent, 78.35.

Per cent of solid, 21.65.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
60°	0.7784	0.7779	49° 10′	1.4337
70°	0.7721	0.7707	49° 46′	1.4301

Calculated for solid :

	n_2.	Molecular refraction.	Theoretical.
60°	1.4206	117.6	
70°	1.4194	117.0	117.2

Distillate, 50 mm. 300° to 302°. $C_{27}H_{56}$.
Per cent of solvent, 82.81.
Per cent of solid, 17.19.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7727	0.7770	49° 50′	1.4297
80°	0.7625	0.7669	50° 13′	1.4272

Calculated for solid :

	n_D.	Molecular refraction.	Theoretical.
70°	1.4287	123.4	
80°	1.4276	126.1	126.4

Distillate, 50 mm. 312° to 314°. $C_{28}H_{58}$.
Per cent of solvent, 79.75.
Per cent of solid, 20.25.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
70°	0.7737	0.7806	49° 42′	1.4305
80°	0.7630	0.7699	50° 15′	1.4277

Calculated for solid :

	n_D.	Molecular refraction.	Theoretical.
70°	1.4285	129.3	
80°	1.4226	129.9	131

Commercial paraffin gave the following indices :
Per cent of solvent, 78.97.
Per cent of solid, 21.03.

	Specific gravity of mixture.	Specific gravity of solid.	Angle for mixture.	n.
60°	0.7784	0.7788	49° 6′ 3″	1.4340
70°	0.7727	0.7732	49° 35′ 6″	1.4311

The results described above show a close agreement in the hydrocarbons separated directly from petroleum, and the corresponding bodies from paraffin, as well as the application of this method for obtaining the molecular refraction of solid bodies.

REPORT.

Moissan's Work on Silicides.

Among the binary compounds made by Moissan and his pupils are the silicides. As some interesting work on this class of compounds has appeared in the *Comptes rendus* during 1902, a report may be welcome. To this report is added a brief notice of the work on silicides by Moissan and his coworkers previous to 1902.

A New Hydride of Silicon.—The hydrides of silicon hitherto described are the gaseous SiH_4, made by Wöhler in 1857[1] by the action of dilute hydrochloric acid on impure magnesium silicide, and the solid yellow $(Si_2H_3)_n$ made by Ogier.[2] It should be noted that pure SiH_4 was first made by Friedel and Ladenburg by the action of sodium on tribasic silicoformic ether.[3]

Moissan and Smiles[4] tried to make pure SiH_4 by preparing the impure gas by Wöhler's method and fractioning it by the process devised by Moissan and Lebeau for separating the fluorides of sulphur.[5] Commercial magnesium powder was treated with ether to remove grease, with a powerful electromagnet to remove particles of iron, dried in a current of hydrogen, and mixed with powdered crystalline silicon made by the method of Vigouroux.[6] By heating this mixture in a current of pure, dry hydrogen a bluish, brittle mass is formed, from which the authors separated the crystalline portion and analyzed it, obtaining percentages close to those required for the compound $SiMg_2$. They consider it, however, to be rather a mixture of metal with one or more silicides. On treating it with dilute hydrochloric acid, a spontaneously inflammable gas escapes, which they prove to be hydrogen mixed with 4 to 5 per cent of SiH_4. Although the gas contained so little silicon hydride, they succeeded in fractioning it. The method depends on the assumption that in a gaseous mixture the constituents will have different freezing-points. In an apparatus filled with hydrogen, the magnesium silicide is decomposed by acid, the resulting mixture of gases washed, dried, and conducted slowly through a U-tube cooled to —180°. At this temperature the hydrides of silicon condense to a solid white mass, while the hydrogen in the mixture escapes. On

[1] Buff and Wöhler: Ann. chim. phys., [3], **53**, 257 (1858).
[2] Ogier: *Ibid.*, [5], **20**, 5 (1880).
[3] Friedel and Ladenburg: *Ibid.*, [4], **23**, 430 (1871).
[4] Moissan and Smiles: Compt. rend., **134**, 569.
[5] Moissan and Lebeau: *Ibid.*, **130**, 865.
[6] Vigouroux: Ann. chim. phys., [7], **12**, 153.

allowing the temperature in the U-tube to rise, the solid hydrides melt, forming a colorless liquid which boils as the temperature rises, giving off pure gaseous SiH_4. A liquid hydride, stable at ordinary temperatures, remains in the tube. The authors repeated this experiment frequently, using magnesium silicide made in several operations, and always obtained the same results.

The liquid hydride boils at 52° and becomes solid at —138°. It takes fire spontaneously in contact with air or with chlorine. It reduces solutions of silver nitrate and mercuric chloride. When a little hydride is vaporized in a vessel filled with hydrogen the latter becomes spontaneously inflammable. Friedel and Ladenburg showed that pure SiH_4 is not spontaneously inflammable. Hence the liquid hydride acts toward SiH_4 as does the liquid phosphine toward the gaseous PH_3, which by contact with air becomes spontaneously inflammable. It is decomposed by solutions of alkalies, forming alkali silicate and hydrogen.

The analysis of the hydride,—decomposition by alkali, or by heat, and measuring the resulting hydrogen,—gave figures suggesting the composition Si_2H_6.

$$Si_2H_6 + 4NaOH + 2H_2O = 2Na_2SiO_3 + 7H_2.$$

In a later article[1] the authors publish the results of a vapor-density determination of the hydride, confirming the composition Si_2H_6. They also give a detailed description of its properties. It can be heated to 100° without decomposition. It is a very energetic reducing agent. It acts curiously on certain saturated chlorides and fluorides. When brought in contact with carbon tetrachloride there is a violent explosion, forming amorphous carbon, amorphous silicon, and hydrochloric acid. Hexafluoride of sulphur is a new substance made by Moissan and Lebeau.[2] It is a gas so stable that sodium can be fused in a vessel filled with it without decomposing the gas. On mixing this gaseous SF_6 with the liquid Si_2H_6 there is a violent explosion, silicon, sulphur, and hydrofluoric acid being formed.

$$SF_6 + Si_2H_6 = S + 2Si + 6HF.$$

Lithium Silicide, Si_2Li_2.—Moissan[3] publishes the results of his attempts to make silicides derived from the hydride Si_2H_6. With potassium or sodium derivatives he was not quite successful, although when he heated either of these metals in a vacuum with silicon, at the boiling-point of the metal very

[1] Moissan and Smiles: Compt. rend., 134, 1549.
[2] Ann. chim. phys., [7], 26, 145.
[3] Moissan: Compt. rend., 134, 1083.

small quantities of silicide were formed. Better success awaited him with lithium. By heating a mixture of silicon with an excess of lithium in a vacuum at a dull red heat, he obtained a mixture of lithium silicide and lithium, from which he removed the lithium by distillation in a vacuum. The lithium silicide was in tiny indigo-blue crystals. Analysis shows it to have the composition Si_2Li_6. It dissociates, when heated in a vacuum, above 600°. Below this temperature hydrogen does not act on it; above 600° hydride of lithium is formed. If the silicide is warmed with fluorine it becomes incandescent, forming lithium fluoride and silicon tetrafluoride. The silicide behaves in much the same way toward chlorine, bromine, iodine, sulphur, and selenium. It is an energetic reducing agent. It exhibits a curious phenomenon when dropped into concentrated sulphuric acid; it becomes incandescent, fuses, and rolls about on the surface of the acid, as does potassium on the surface of water. The sulphuric acid is reduced to hydrogen sulphide and sulphur. When brought in contact with dilute acid or water it is violently attacked, forming a mixture of spontaneously inflammable hydride of silicon and hydrogen. But if means are taken to render the action of water very slow only hydrogen escapes. The explanation is that in the violent action Si_2H_6 is formed but decomposes mostly into SiH_4, H_2, and alkali silicate, while if the action is slow the reaction is

$$Si_2Li_6 + 6H_2O = Si_2H_6 + 6LiOH.$$

But as alkali decomposes the hydride, we get

$$4LiOH + Si_2H_6 + 2H_2O = 2Li_2SiO_3 + 7H_2.$$

Cerium Silicides.—Ulik,[1] in 1865, while electrolyzing cerium fluoride, obtained a substance to which he assigned the composition Ce_2Si. Sterba,[2] working with Moissan, has studied the action of silicon on cerium oxide in varied proportions in the electric furnace. A definite crystalline substance of the composition $CeSi_2$ was the invariable result. This silicide crystallizes in opaque, steel-colored, brittle, microscopic crystals, is insoluble in water, does not react with hydrogen, reacts with oxygen or air only at high temperatures, reacts with cold fluorine with incandescence, and when warmed with chlorine, bromine, iodine, sulphur, or selenium, reacts with incandescence. It is attacked by hydrochloric and hydrofluoric acids.

[1] Ulik: Chem. Centrb., 1865, p. 1045.
[2] Sterba: Compt. rend., 135, 170.

Cobalt Silicides.—Vigouroux,[1] in 1897, described a silicide of the composition $SiCo_2$, obtained by melting 10 parts of cobalt with 1 part of silicon. Its preparation and its properties recall those of the ferrous silicide, $SiFe_2$, studied by Moissan in 1895.[2] Lebeau,[3] in 1901, prepared a silicide, SiCo, by the action of copper silicide on cobalt at high temperatures, which resembled in its properties the iron silicide, SiFe. SiCo, like SiFe, can be dissociated, forming free silicon and $SiCo_2$. These analogies led Lebeau[4] to try to make a silicide, Si_2Co, to correspond with the third silicide of iron, Si_2Fe. He succeeded in preparing Si_2Co by heating cobalt with an excess of silicon, but he obtained it better crystallized by the action of copper silicide on a mixture of cobalt and silicon in the electric furnace. Si_2Co is obtained in small, dark-blue, octahedral crystals, which seem to belong to the regular system. It is a very stable substance, not attacked by oxygen, by nitric, sulphuric, or hydrochloric acids, or by alkalies. Hydrofluoric acid dissolves it, and fluorine changes it to CoF_2 and silicon tetrafluoride.

Previous Work on Silicides by Moissan and Co-workers.

Moissan: Compt. rend., **117**, 425. Silicide of carbon, CSi.

" *Ibid.*, **119**, 1172. Fused iron carbide treated with silicon gives iron silicide and graphite.

Lévy: *Ibid.*, **121**, 1148. Titanium silicide, $SiTi_2$, by the action of titanium chloride on silicon at high temperatures.

Vigouroux: *Ibid.*, **121**, 711. Manganese silicide, $SiMn_2$, by the union of the elements in the electric furnace.

Vigouroux: *Ibid.*, **121**, 686. Nickel silicide, $SiNi_2$, and cobalt silicide, $SiCo_2$, by the union of the elements in the electric furnace.

Moissan: *Ibid.*, **121**, 621. Iron silicide, $SiFe_2$, chromium silicide, $SiCr_2$, by the union of the elements in the electric furnace.

Vigouroux: *Ibid.*, **122**, 318. Copper silicide, $SiCu_2$, by the union of the elements in the electric furnace.

Vigouroux: *Ibid.*, **123**, 116. Platinum silicide, $SiPt_2$. He finds that silicon does not combine directly with aluminium, lead, tin, antimony, bismuth, gold, or silver. He tried temperatures up to the volatilization of each metal.

Zettel: *Ibid.*, **126**, 833. Chromium silicide, $SiCr_2$, gray crystalline powder.

[1] Vigouroux: Ann. chim. phys., [7], **12**, 153; Compt. rend., **121**, 686.
[2] Moissan: Compt. rend., **121**, 621.
[3] Lebeau: *Ibid.*, **132**, 556.
[4] Lebeau: *Ibid.*, **135**, 475.

Lebeau : *Ibid.*, **128**, 1642. Iron silicide, SiFe, by the action of copper silicide on iron. This silicide was first made by Fremy by the action of silicon tetrachloride on iron.

Vigouroux : *Ibid.*, **129**, 1238. Molybdenum silicide, Si_3Mo_2, by the action of silicon on molybdenum oxide in the electric furnace.

Lebeau : *Ibid.*, **131**, 583. Silicon present as $SiFe_2$ in commercial ferrosilicon.

Moissan and Stock : *Ibid.*, **131**, 139. Silicon borides, SiB_3, SiB_6, from boron and silicon in the electric furnace.

Lebeau : *Ibid.*, **133**, 1008. Silicon is present in pig-iron as $SiFe_2$. E. R.

REVIEWS.

LEHRBUCH DER ANORGANISCHEN CHEMIE. By PROFESSOR DR. HUGO ERDMAN. 3rd edition. Braunschweig : Vieweg und Sohn. 1902.

The speedy appearance of 3,000 more copies of this work furnishes renewed evidence that in the popular mind its virtues exceed its defects. The new edition is essentially similar to the preceding, and the reader is referred to the reviews already published concerning them.[1] The new page (18) concerning force and work is very welcome, but it might have been amplified with advantage in a chemical direction. The few words concerning the Phase Rule and the Law of Guldberg and Waage (pp. 135 and 731) do little to relieve the inadequacy of the theoretical treatment. To those familiar with the somewhat wearisome discussion concerning the standard of atomic weights, it will be no surprise to learn that Erdmann continues to reject the excellent list prepared by his eminent compatriots; but many will be surprised to see the atomic weights of all elements given with two decimal places. This proceeding, of course, implies that the value for tantalum, for example, is known over ten times as accurately as that for oxygen, the numbers given being respectively 181.45 and 15.88.

On the other hand, it is probable that no other book of the same size records so great a variety of interesting experimental facts concerning inorganic substances. T. W. R.

CELLULAR TOXINES, OR THE CHEMICAL FACTORS IN THE CAUSATION OF DISEASE. By VICTOR C. VAUGHAN, M.D., LL.D., Professor of Hygiene and Physiological Chemistry and director of the Hygienic Laboratory in the University of Michigan, and FREDERICK G. NOVY, M.D., Sc.D., Junior Professor of Hygiene and Physiological Chemistry in the University of Michigan. Fourth edition. Philadelphia and New York : Lea Brothers & Co. 1902. 495 pp.

The fact that this is the fourth edition of this work since

[1] This JOURNAL, **20**, 847 (1898); **23**, 250 (1901).

1888 shows that the book has received the appreciation it deserves. It also gives a slight indication of the great progress that is being made in this line of work. Of necessity many changes have been made in this edition and much valuable matter added. The subject-matter has been brought up to 1902. The subjects now attracting the greatest amount of attention, namely, the theory of immunity, the specific precipitins and agglutinins, and the various cytolysins are lucidly discussed.

In connection with the theory of cytolysis, Ehrlich's graphic representations of the union of receptor, intermediary body, and complement are reproduced. The chemist is certain to be amused by these diagrams representing the union of supposedly definite chemical substances.

It must be remembered, however, that the diagrams were introduced merely to bring out clearly the relationship which is believed to exist between these bodies. The large amount of work which Ehrlich's theory has called forth has supported the theory and amply justified its promulgation.

The last two thirds of the book is devoted to food poisoning and the chemistry of the ptomains and leucomains, to the literature of which the authors have contributed much. Most of the excellent bibliography of the previous edition has been omitted on account of lack of space. This is, of course, to be regretted. The references to the very recent work are given, however.

The book is of great value because of the importance of the subject-matter, which is well handled throughout. The original communications in this field are so scattered in the literature, and the nomenclature is so involved, that it is well-nigh impossible for those who are not working along these lines to keep up with the literature without the aid of such a book. It is the only book on the subject that is at all comprehensive, and should be within reach of all who are interested or working in this field of investigation. A. S. L.

HIGHER MATHEMATICS FOR STUDENTS OF CHEMISTRY AND PHYSICS, WITH SPECIAL REFERENCE TO PRACTICAL WORK. By J. W. MELLOR, D.Sc., late Senior Scholar and 1851 Exhibition Scholar, New Zealand University; Research Fellow, The Owens College, Manchester. London, New York, and Bombay: Longmans, Green & Co. 1902.

The appearance of the admirable work in hand is most timely. If chemical students have a need which surpasses all others it is the need for at least an elementary knowledge of the higher mathematics. The day is past when this can be omitted from the training of a chemist.

While this is true, it must, however, not be forgotten that

there is a limit to the capacity and time of even the best students. The requirements to-day, of a student of chemistry, are not few in number. In addition to being a fair linguist he must have a close acquaintance with general physics, and if we expect him, in addition, to follow a long and elaborate course in differential and integral calculus and differential equations, we usually find that our expectations are disappointed. The object of the author can be seen best by quoting from his preface: "It is almost impossible to follow the later developments of physical or general chemistry without a working knowledge of higher mathematics. I have found that the regular text-books of mathematics rather perplex than assist the chemical student who seeks a short road to this knowledge, for it is not easy to discover the relation which the pure abstractions of formal mathematics bear to the problems which every day confront the student of nature's laws, and realize the complementary character of mathematical and physical processes.

"This work starts from the thesis that, so far as the investigator is concerned, higher mathematics is the art of reasoning about the numerical relations between natural phenomena; and the several sections of higher mathematics are different modes of viewing these relations."

The "elementary" part of the book treats of the differential calculus, coordinate or analytical geometry, functions with singular properties, the integral calculus, and infinite series and their uses.

The "advanced" portion deals with hyperbolic functions, how to solve differential equations, and Fourier's theories.

Under "useful results" we find chapters on how to solve numerical equations, determinants, probability and the theory of errors, a collection of formulas for reference, and reference tables.

The work is more than excellent, and is by far the best which has appeared in this field. It can not only be unconditionally recommended to all students of chemistry, but they are ardently urged to carefully study it if they wish to be able to follow the more recent developments in the theoretical side of their science. H. C. J.